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DEVELOPMENT OF FLEXIBLE POLYMERS
AS THERMAL INSULATION IN SOLID-
PROPELLANT ROCKET MOTORS
Second Annual Summary Report

ROCK ISLAND ARSENAL
ROCK ISLAND, ILLINOIS

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ATLANTIC RESEARCH
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ATLANTIC RESEARCH CORPORATION
ALEXANDRIA, VIRGINIA

DEVELOPMENT OF FLEXIBLE POLYMERS
AS THERMAL INSULATION IN SOLID-
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Second Annual Summary Report

June 30, 1961 to June 30, 1962

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ABSTRACT

Several new flexible epoxy resins were prepared using internal modifiers. The flexibilization of the Guardian resin and of a liquid novolac epoxy resin with Thiokol LP-8 was successful. Other flexible epoxy resins developed were Araldite DP-437-tetrahydrophthalic anhydride, Epon 828-tetrahydrophthalic anhydride-castor oil, silicon diepoxide QZ-8-0914-Nadic methyl anhydride, and silicon diepoxide QZ-8-0914-Nadic methyl anhydride-castor oil formulations. A flexible phenolic resin based on a commercially available "Stage A" phenol-formaldehyde resin and Syl-Kem 90 was developed. A few flexible melamine resins were developed, but most of the reactions attempted with melamine and methanol melamines were unsuccessful. The modification of diallyl melamine with Syl-Kem 90 and of dimethylol diallyl melamine with Thiokol LP-8 resulted in a flexible and a slightly flexible melamine resin, respectively. Triglycidyl cyanurate was successfully prepared and modified with Thiokol EM-207 to yield a flexible resin. A flexible polyurethane resin was prepared from toluene diisocyanate and castor oil. A preliminary study of furan resins was started. Several organic acid catalysts and liquid polysulfides were investigated. A flexible resin was obtained with a mixture containing furiuryl alcohol (or the aldehyde), phenolic resin, and Syl-Kem 90.

Based on insulation performance and density, the optimum amount of asbestos fiber in the castor oil-modified Guardian was found to be 40 per cent. Attempts to fill a flexible melamine resin with asbestos fibers were unsuccessful. Other fillers were investigated for several of the better-performing flexible epoxy and phenolic resins. The use of an asbestos-potassium oxalate composite filler resulted in lower char rates for a flexible epoxy and a flexible phenolic resin than when these two resins contained only asbestos. Potassium oxalate and magnesium carbonate by themselves were inferior to asbestos.

Two externally plasticized resins, Guardian modified with 50 per cent dibutyl maleate or 50 per cent Aroclor 1248, were found to be unacceptable because of extensive changes in mechanical properties on aging for one year at ambient.

Mechanical properties were compared between the Syl-Kem 90-modified phenol-formaldehyde resin prepared in our laboratory and the Syl-Kem 90-modified commercially available stage A phenol-formaldehyde resin. The commercially available material yielded resins with lower tensile strengths (100 to 300 psi versus 1,000 to 3,000 psi) and higher elongations at resin contents between 40 and 50 per cent, but lower elongations at resin contents between 30 and 35 per cent.

Oxyacetylene-torch testing has shown the following asbestos-filled resins to have good insulating properties: Epon 815 modified with XR2000, Guardian modified with castor oil, Oxiron 2000 modified with Empol 1014, a standard phenolic-formaldehyde stage A resin modified with Syl-Kem 90, and a nonyl phenolic-formaldehyde stage A resin modified with Syl-Kem 90. Oxyacetylene-torch test data showed that 2 or 3 layers of Pluton cloth on the exposed face of 40 per cent asbestos-filled Guardian resulted in a marginal increase in insulation effectiveness.

Flexible epoxy, phenolic, and urethane resins have been tested in the convergent and peripheral sections of static motors. The better-performing asbestos-filled materials had the following char rates (the values in parentheses are for one of the best commercially available insulation materials, U. S. Rubber 3015, tested at the same time): 40-per cent-castor oil-modified Guardian, 3.0 mil/sec (3.2); Araldite DP-437 modified with Nadic methyl anhydride, 2.4 mil/sec (2.6); nonyl phenolic-formaldehyde resin modified with Syl-Kem 90, 2.7 mil/sec (2.6); standard phenolic-formaldehyde resin modified with Syl-Kem 90, 2.6 mil/sec (2.3). When this phenolic-Syl-Kem 90 formulation was filled with a composite filler composed of equal amounts of asbestos fiber and potassium oxalate, the char rate was reduced to 2.1 mil/sec (3.1). When the 40-per cent-castor oil-modified Guardian was filled with a composite filler composed of 2 parts oxalate and 1 part asbestos powder, the calculated char rate was 1.3 mil/sec. The lowest char rate obtained for a polyurethane resin was 4.1 mil/sec (3.2).

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Other conclusions based on a limited number of motor firings are that (1) Epon 815 can be substituted for Epon 828 in the castor oil modifications of Guardian with perhaps some improvement in insulation performance. Varying the Epon 828 in the castor oil-modified Guardian formulation appears as effective as varying the Nallic methyl anhydride. The use of Thiokol LP-8 in place of castor oil to flexibilize the Guardian resulted in a material of approximately the same char rate.

TABLE OF CONTENTS

| | <u>Page</u> |
|---|-------------|
| I. INTRODUCTION | 1 |
| II. RESULTS AND DISCUSSION | 2 |
| A. EPOXY RESINS | 2 |
| 1. Flexibilization | 2 |
| a. Modification of Epoxy Resins with Tetrahydrophthalic Anhydride | 2 |
| b. Formulations Based on Epoxy Silicone Resin QZ-8-0914 | 6 |
| c. Formulations Based on a Novolac Epoxy Resin (Epiphen 825) | 7 |
| d. Castor Oil Modifications | 7 |
| e. Modification of Guardian with Thiokol LP-8 | 8 |
| f. Formulations Based on Irochemrez 444 Epoxy Resin | 8 |
| 2. Fillers | 10 |
| 3. Mechanical Testing | 11 |
| 4. Oxyacetylene-Torch Testing | 15 |
| 5. Static-Motor Firing Tests | 20 |
| a. Convergent-Section Testing | 22 |
| b. Peripheral-Slab-Section Testing | 22 |
| c. Discussion of Motor-Firing Tests | 40 |
| B. MELAMINE RESINS | 45 |
| 1. Flexibilization | 45 |
| a. Co-Polymerization of Melamine or Methylol Melamine with Polyepoxides | 45 |
| b. Co-Polymerization of Dimethylol Melamine with a Polyamide | 46 |
| c. Co-Polymerization of Melamine with Polybasic Acids | 46 |
| d. Co-Polymerization of Methylol Melamines with Polyols | 47 |
| e. Co-Polymerization of Methylol Melamine with Polythiols | 48 |
| f. Co-Polymerization of Melamines with Isocyanates | 49 |
| g. Attempted Preparation of N ² , N ⁴ , N ⁶ -Trihexylamine Melamine | 50 |
| h. Preparation of Triphenyl Cyanurate and Attempted Preparation of N ² , N ⁴ , N ⁶ -tris-(β -hydroxyethyl)-Melamine | 51 |
| i. Preparation and Polymerization of Triglycidyl Cyanurate | 52 |
| j. Reaction of Dimethylol Melamine with Polyvinyl Acetal Resins | 54 |

TABLE OF CONTENTS (Cont.)

| | | |
|------|---|-------------------|
| | 2. Preparation of Filled Melamine Resins | <u>Page</u> 56 |
| C. | FLEXIBLE PHENOLIC RESINS | 56 |
| | 1. Determination of Physical Properties | 56 |
| | 2. Oxyacetylene-Torch Test Results | 58 |
| | 3. Static-Motor Testing | 60 |
| D. | POLYURETHANE RESINS | 67 |
| | 1. Internal Flexibilization of Polyurethane Resins | 67 |
| | 2. Oxyacetylene-Torch Testing of Filled Urethane Resins | 67 |
| | 3. Motor Firing Tests of Filled Polyurethane Resins | 69 |
| E. | FURAN RESINS | 69 |
| III. | SUMMARY OF INSULATION WORK | 73 |
| IV. | FUTURE WORK | 76 |
| | APPENDIX | |

LIST OF FIGURES

| <u>Figure</u> | <u>Title</u> | <u>Page</u> |
|---------------|--|-------------|
| 1 | Shore A-2 Hardness as a Function of NMA-Castor Oil Precooking Time (Modified Guardian) | 9 |
| 2 | Relationship of Density and Asbestos Content for 40- Per Cent, Castor Oil Modified Guardian | 13 |
| 3 | Cross Section of End-Burning Solid-Propellant Rocket Motor | 21 |
| 4 | Test Specimens in the Convergent-Section Before Motor Firing | 23 |
| 5 | Test Specimens in the Convergent-Section After Motor Firing | 24 |
| 6 | Convergent-Section Test Specimens from Firing M-298 | 30 |
| 7 | Convergent-Section Test Specimens from Firing M-30 | 30 |
| 8 | Convergent-Section Test Specimens from Firing PYB-8 | 30 |
| 9 | Test Specimen in the Peripheral-Slab Section Before Motor Firing | 31 |
| 10 | Peripheral-Slab Test Specimens from Firing PYM-3 | 36 |
| 11 | Peripheral-Slab Test Specimens from Firing M-284 | 37 |
| 12 | Peripheral-Slab Test Specimens from Firing B-35 | 38 |
| 13 | Peripheral-Slab Test Specimens from Firing B-68 | 39 |
| 14 | Convergent-Section Test Specimens from Firing PYB-5 | 61 |
| 15 | Convergent-Section Test Specimens from Firing M-299 | 61 |

LIST OF TABLES

| <u>Table</u> | <u>Title</u> | <u>Page</u> |
|--------------|---|-------------|
| I | Internal Flexibilization of Epoxy Resins | 3 |
| II | Preparation of Filled Epoxy Resins | 12 |
| III | Aging Studies on Externally Plasticized Guardian | 14 |
| IV | Oxyacetylene Torch-Test Results for Asbestos-Filled Epoxy Resins | 17 |
| V | Oxyacetylene Torch-Test Results for Asbestos-Filled Epoxy Resins | 18 |
| VI | Oxyacetylene Torch-Test Results for Filled Epoxy Resins | 19 |
| VII | Convergent-Section Motor Firing M-275 Results for Filled Epoxy Resins | 25 |
| VIII | Convergent-Section Motor Firing B-16 Results for Filled Epoxy Resins | 26 |
| IX | Convergent-Section Motor Firing M-298 Results for Filled Epoxy Resins | 27 |
| X | Convergent-Section Motor Firing M-300 Results for Filled Epoxy Resins | 28 |
| XI | Convergent-Section Motor Firing PYB-8 Results for Filled Epoxy Resins | 29 |
| XII | Peripheral-Slab Motor Firing PYM-3 Results for Filled Epoxy Resins | 32 |
| XIII | Peripheral-Slab Motor Firing M-284 Results of Filled Epoxy Resins | 33 |
| XIV | Peripheral-Slab Motor Firing B-35 Results for Filled Epoxy Resins | 34 |
| XV | Peripheral-Slab Motor Firing B-68 Results for Filled Epoxy Resins | 35 |
| XVI | Comparison of Char Rates of Guardian Modifications Containing 40 Per Cent Asbestos Fiber | 41 |
| XVII | Comparison of Char Rates of New Flexible Epoxy Resins Containing 40 Per Cent Asbestos Fiber | 43 |

LIST OF TABLES (Cont.)

| | | <u>Page</u> |
|--------|---|-------------|
| XVIII | Modifications of Triglycidyl Cyanurate | 55 |
| XIX | Physical Properties of Modified Bakelite B2620 and Standard Phenolic Resins | 57 |
| XX | Oxyacetylene Torch-Test Results for Asbestos-Filled Phenolics | 59 |
| XXI | Convergent-Section Motor Firing M-282 Results for Filled Phenolic Resins | 62 |
| XXII | Convergent-Section Motor Firing PYB-5 Results for Filled Phenolic Resins | 63 |
| XXIII | Convergent-Section Motor Firing M-299 Results for Filled Phenolic Resins | 64 |
| XXIV | Convergent-Section Motor Firing M-300 Results for Filled Phenolic Resins | 65 |
| XXV | Comparison of Char Rates of a Flexible Phenolic Resin Containing Various Fillers | 66 |
| XXVI | Oxyacetylene Torch Test Results for Filled Polyurethane Resins | 68 |
| XXVII | Peripheral-Slab Motor Firing of Asbestos-Filled Polyurethane Resins (Firing B-35) | 70 |
| XXVIII | Acid Catalysis of Furfuryl Alcohol Polymerizations | 72 |
| XXIX | Summary of Best Insulation Developed to Date Under This Program | 75 |

I. INTRODUCTION

The purpose of thermal insulation is to prevent excessive heating of the structural parts of a missile by the burning propellant. The insulation must be sufficiently flexible to conform to the shape of the structural parts which strain elastically under high operational pressure. If the insulation does not elongate adequately, it fractures, and the hot propellant gases penetrate to the motor case to cause overheating and failure. When the insulation is bonded to the grain or to the motor case, flexibility is essential to prevent fracture of the bond and possible motor failure by side burning..

The purpose of this project is to develop flexible polymers, which, when combined with appropriate fillers, will be suitable for use as thermal insulation in solid propellant rocket motors. Polymeric systems selected for investigation are epoxies, phenolics, melamines, furans, polyurethanes, and polyesters. The investigation includes the modification of commercially available resins, the synthesis of new polymers, and the correlation of polymer structure with performance.

II. RESULTS AND DISCUSSION

A. EPOXY RESINS

1. Flexibilization

During this report period work was continued on the preparation of flexible epoxy resins having potentially good insulation characteristics. Emphasis was placed on introducing flexibility with internal modifiers; that is, modifiers that chemically react with the epoxy resin as opposed to the usual plasticizers which simply form a solid solution with the resin. The results are summarized in Table I. The relative terms rigid, slightly flexible, flexible, and very flexible permit qualitative comparisons. A rigid material does not bend under a manually applied force and usually breaks without plastic, or significant elastic deformation. A slightly flexible material bends slightly, in the range of 5 to 30 degrees, without breaking. A flexible material can be bent 180 degrees with moderate manual force. The very flexible materials were quite easily bent 180 degrees with very little force, almost elastomeric in characteristic. These observations were made on approximately 4-mm-thick unfilled specimens which were prepared by casting 9 to 10 grams of the modified resins in aluminum weighing dishes.

a. Modification of Epoxy Resins with Tetrahydrophthalic Anhydride (THPA)*

Previous work at Atlantic Research Corporation on epoxy-anhydride resin systems had resulted in the development of an asbestos-filled resin composed of 10 parts Epon 828 and 9 parts TPHA with excellent insulation performance in static motor firing. Seven motor firings gave an average char rate of 2.2 mil/sec. This cured material is, however, rigid. Furthermore, TPHA is a solid (melting point 100°C) and is not very soluble in the epoxy resin at room temperature, resulting in molding problems. It was hoped that the TPHA would be very soluble

* Abbreviations and structures are listed in the Appendix.

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Table I

Internal Flexibilization of Epoxy Resins

| Formulation Number | Formulation ^a (ratio of parts by weight) | Cure Conditions | | Results |
|--------------------|--|---------------------|--------------|---|
| | | Temperature (°C) | Time (hr) | |
| 117-I | Epon 828 ^b /NMA/castor oil 1.00:1.17:1.17 (35%) ^c | 125 | 18 | Flexible |
| 117-II | Epon 815/NMA/castor oil 1.00:1.17:1.17 (35%) ^c | 125 | 18 | Flexible |
| Series 129 | Epon 828/NMA/Thiokol LP-8 | | | |
| 129-I | 1.0:0.88:0.21 (10%) ^d | 125 | 1 | Rigid |
| 129-II | 1.0:0.90:0.47 (20%) ^d | 125 | 1 | Rigid |
| 129-III | 1.0:0.91:0.82 (30%) ^d | 125 | 1 | Very slightly flexible. |
| 129-IV | 1.0:0.93:1.29 (40%) ^d | 125 | 1 | Flexible |
| Series 138 | Epiphen 825/Thiokol LP-8 | | | |
| 138-I | 2:1 | 130 | 6 | Slightly flexible; brittle. |
| 138-II | 1:1 | 130 | 6 | Very flexible; low tensile strength. |
| 138-III | 1:2 | 130 | 1.5 | Very flexible; low tensile strength; broke on bending 180 degrees. |
| 141-I | Epiphen 825/NMA 10:9 | 120 | 1 | Rigid |
| 141-II | Epiphen 825/NMA/castor oil | | | |
| | 1.0:1.1:0.91 (30%) ^c | 120 | 2 | Incompatible |
| | 1.0:1.3:1.6 (40%) ^c | 120 | 2 | Incompatible |
| 146-I | Araldite DP-437/NMA/THPA 1.00:0.30:0.60 | 130 | 1 | Slightly flexible. |
| Series 147 | Araldite DP-437/THPA | | | |
| 147-I | 1.0:0.38 | 130 | 1 | Very flexible. |
| 147-II | 1.0:0.90 | 130 | 1.5 | Initially flexible, but hardened and became brittle on standing. |
| Series 153 | QZ-8-0914/NMA | | | |
| 153-I | 2.0:1.0 | 125 | 0.75 | Very flexible; low tensile, broke on bending 180 degrees. |
| 153-II | 1.0:1.0 | 125 | 0.75 | Flexible, but hardened on standing overnight to slightly flexible. |
| 153-III | 1.0:2.0 | 125 | 0.75 | Flexible |
| Series 156 | QZ-8-0914/NMA/castor oil | | | |
| 156-I | 1.00:0.88:0.21 (10%) ^c | 125 | 1.33 | Flexible |
| 156-II | 1.00:0.90:0.47 (20%) ^c | 125 | 1.33 | Very flexible. |
| 156-III | 1.00:0.91:0.82 (30%) ^c | 125 | 2 | Very flexible; slightly tacky. |
| 156-IV | 1.00:0.93:1.27 (40%) ^c | 125 | 2 | Very flexible; slightly tacky. |
| 157-I | Epon 828 THPA/castor oil (1:1) ^e (35%) 3.0:7.0 | 125 | 1.5 | Flexible |
| 158-I | Isochemrez 444 ^f / Isochemrez Hardener No. 6 10:0.80 | 100 | 1 | Hard, rigid; foamed. |

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Table I (Cont'd)

| Formulation Number | Formulation ^a (ratio of parts by weight) | Temperature (°C) | Time (hr) | Results |
|--------------------|--|---------------------|--------------|---------------------------------|
| 158-II | Isochemrez 444 ^f / Isochem Hardener No. 44 10:1.5 | 100 | 1 | Hard, rigid. |
| 158-III | Isochemrez 444 ^f / Isochem Hardener No. 44/ EM 207 5.0:0.75:5.0 | 100 then 125 | 1 2 | Flexible; low tensile strength. |
| 158-IV | Isochemrez 444 ^f / Isochem Hardener No. 44/ castor oil 7.0:1.0:3.0 | 100 | 1 | Rigid, brittle. |
| 160-I | Epon 828 THPA/castor oil (1.0:1.39) ^g (42%) ^c 2.8:7.2 | 125 | 2 | Very flexible. |

- a. All cures catalyzed by 2.0 per cent benzyldimethyl amine (BDMA) unless otherwise noted (footnote f).
b. Materials described in Appendix.
c. Per cent castor oil.
d. Per cent Thiokol LP-8.
e. THPA and castor oil pre-reacted at 125°C for 20 hours and then for an additional 24 hours after adding 2.0 per cent BDMA before use in this formulation.
f. Commercial epoxy resin containing ceramic microballoons. No BDMA used in these formulations.
g. THPA, castor oil, and 0.7 per cent by weight of BDMA were pre-reacted at 125°C for several days before use in this formulation.

in the liquid Nadic methyl anhydride (NMA) at room temperature. If a solution consisting of 60 to 80 per cent of THPA and 40 to 20 per cent NMA could be prepared, the THPA would be much easier to handle, and perhaps just as effective in imparting good thermal insulation characteristics to the epoxy resins as the pure THPA. It was found that more than 2 parts of THPA could be dissolved in 1 part of NMA at elevated temperatures. However, even on cooling a 50-per cent solution to room temperature, THPA crystallized out. Formulation 146-I represents an attempt to use a solution of THPA in NMA to modify Araldite DP 437. However, if this three-component mixture was allowed to cool, phase separation occurred.

A second approach to obtain a convenient THPA formulation was based on the following reasoning. Since (1) the flexible, asbestos-filled, castor oil-modified, Guardian* formulation has proved to be one of the best insulators developed to date under this contract, and (2) the replacement of NMA by THPA in the Guardian results in an excellent performing, rigid insulation, the replacement of NMA by THPA in the flexible, castor oil-modified Guardian formulation was considered. Furthermore, there appears to be no difference in the insulation performance of a 30-per cent-castor oil-modified Guardian formulation that has been prepared by first reacting NMA with castor oil for several hours at 150°C and then adding Epon 828, and one that has been prepared by mixing all three components (Epon 828-NMA-castor oil) together at the beginning. By prereacting the castor oil with THPA, it was hoped that a liquid co-reactant would be obtained which could be readily mixed at room temperature with the Epon 828 (and asbestos) and thus avoid the difficulty of working with the solid THPA itself.

Equal parts of THPA and castor oil were heated together at 125°C for 18 hours. On cooling a sample of this material, a milky, semi-solid paste formed when it was agitated with a glass rod. Then approximately 2 per cent of benzyldimethyl amine (BDMA) was added to the main solution and heating continued. After 5 hours, a paste would

* Guardian consists of 10 parts Epon 828 and 9 parts Nadic methyl anhydride, with 2 per cent of benzyldimethyl amine added.

still form at room temperature, but by the end of 21 hours, a very viscous liquid which did not solidify was obtained. To this viscous liquid was added a sufficient amount of Epon 828 to yield a modified resin (formulation 157-I) containing 35 per cent castor oil. In a similar manner, formulation 160-I was prepared in which the concentration of castor oil was increased to 42 per cent. In both cases a flexible material resulted. Since Araldite DP-437 is an inherently flexible epoxy resin, its modification with THPA to improve performance as an insulator was investigated. In formulation 147-II, Araldite DP-437 and the THPA were used in the same weight ratio as Epon 828 and NMA in the Guardian formulation; while in formulation 147-I, the ratio of DP-437 to THPA was equal to the equivalent stoichiometry ratio of Epon 828 to NMA in the Guardian formulation. In these two formulations, the THPA would crystallize out if the solution were allowed to cool before it cured. Formulation 147-I yielded a very flexible resin and is worthy of further investigation, while 147-II yielded a resin which hardened and became brittle on standing overnight. It may also be possible, and desirable, to increase the amount of THPA to a more significant level than that used in formulation 147-I.

b. Formulations Based on Epoxy Silicone Resin QZ-8-0914

Series 153 and 156 are some initial studies in the modification of Dow Corning's difunctional epoxy-silicone resin, QZ-8-0914. This resin is a technical grade of Syl-Kem 90. We have used both Syl-Kem 90 and QZ-8-0914 in the flexibilization of melamine and phenol-formaldehyde resins, of which some of the latter have shown very good insulation performance. Therefore, the modification of this type of epoxy resin with modifiers that have yielded flexible epoxy resins exhibiting good insulation performance was studied. The 156 series is equivalent to the castor oil-modified Guardian formulation except that Epon 828 is replaced by the diepoxide QZ-8-0914. The 10-, 20-, 30-, and 40-per cent-castor oil modifications were all flexible and appear worthy of continued investigation.

In the 153 series, QZ-8-0914 was modified with various amounts of NMA. Formulation 153-III (1:2 ratio) was flexible and had good tensile strength. The other formulations lacked flexibility or good tensile strength.

c. Formulations Based on a Novolac Epoxy Resin (Epiphen 825)

Most epoxy formulations in these studies have been with the bis-phenol A-epichlorohydrin and the epoxidized aliphatic-polyolefin types of resins. Since the novolac epoxy resins have a structure similar in many respects to the "Stage A" phenol-formaldehyde resin and since the phenolic resins generally have good insulation properties, the preparation of a flexible novolac epoxy resin was investigated.

The modification of Epiphen 825 with the liquid polysulfide LP-8 resulted in a very flexible material. However, attempts to substitute Epiphen 825 for Epon 828 in the 30- and 40-per cent-castor oil-modified Guardian were unsuccessful. Although the Epiphen 825, NMA, and castor oil yielded a homogeneous solution at the cure temperature, the Epiphen 825 appeared to homopolymerize to a rigid material with incorporation of practically no castor oil into the polymeric structure.

d. Castor Oil Modifications

It was previously reported* that to completely satisfy the stoichiometry of a cross-linked Guardian formulation modified with castor oil, more of either NMA or Epon 828, or both, is added to react with the hydroxyl groups in the castor oil. Also, it was indicated that a more flexible material results if NMA is first heated with the castor oil and then cured with Epon 828 as a separate step.

A resin was prepared from Epon 828 and a pre-cooked (5 hours at 130°C) mixture of castor oil and NMA. BDMA served as catalyst. Another resin was prepared using this same procedure except that Epon 815 replaced Epon 828. The results are summarized in formulations 117-I and 117-II, respectively. Although these two formulations yielded moderately

* First Annual Summary Report, Contract DA-36-034-ORD-3325 RD, July 24, 1961, p. 18.

flexible materials, the fact that greater flexibility did not result was attributed to either the long over-cure of about 15 hours or the "pre-cooking" for 5 hours of the NMA and castor oil, or both.

To determine the effect of "pre-cook" time on resin flexibility, 35-per cent-castor oil-modified Guardian specimens were prepared in which the NMA-castor oil mixtures were pre-cooked for different lengths of time at 130°C. The specimens were then cured at 125°C for 3 hours with the proper amount of Epon 828. Shore hardness was determined for the cured materials. The results, summarized in Figure 1, indicate an optimum pre-cooking time of between 15 and 30 minutes to achieve minimum hardness for a completely cured material.

However, it should be emphasized that NMA and castor oil are pre-cooked not only to obtain greater flexibility, but also to improve the compatibility of castor oil with Epon 828 and NMA. Thus, in the case of 40-per cent-castor oil-modified Guardian, this technique is necessary to obtain a good molding based on this formulation. Unfortunately, maximum compatibility is obtained only after 180 minutes of pre-cooking at 130°C, which, as can be seen from Figure 1, does not yield a material of minimum hardness. Nevertheless, flexibility of the final material is still quite adequate.

e. Modification of Guardian with Thiokol LP-8

Because of the success with castor oil in the modification of the Guardian to a good, flexible insulator, other modifiers were sought which might prove to be even more effective. It was found that LP-8 is an effective flexibilizer for the Guardian (series 129) at a concentration of approximately 40 per cent. The pot life of this formulation is in excess of 6 hours and thus quite adequate for the preparation of asbestos-filled moldings.

f. Formulations Based on Isochemrez 444 Epoxy Resin

Isochemrez 444, a commercially available material described as a "ceramic-microballoon-filled, high-temperature-stable", epoxy resin,

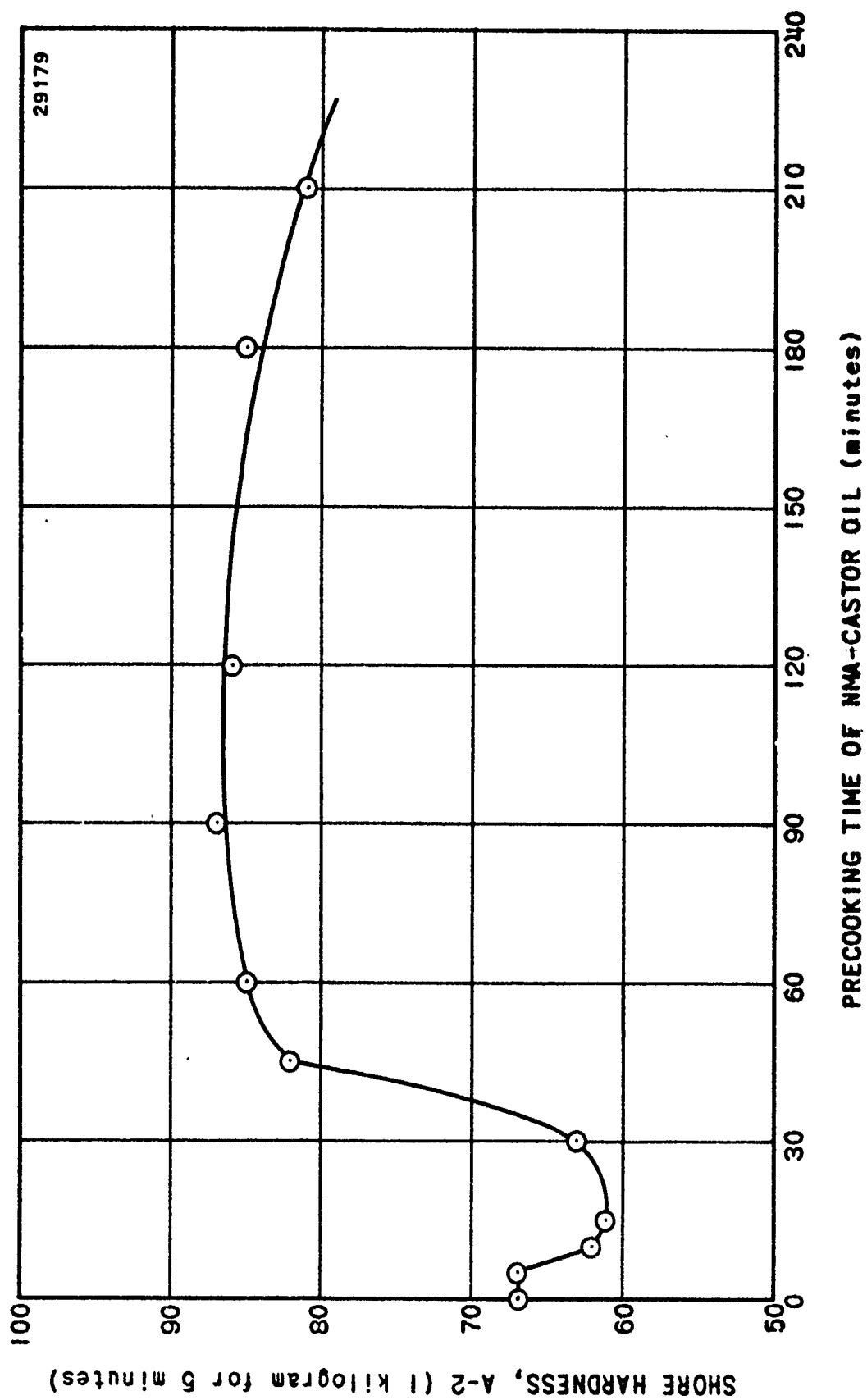


Figure 1. Shore A-2 Hardness as a Function of NMA-Castor Oil Precooking Time (Modified Guardian).

is of interest because of its extremely low density, 0.67 gm/cc. Since the curing agents recommended for this system by the supplier yield rigid materials (formulations 158-I, II), the introduction of flexibility with castor oil and Thiokol EM 207 was investigated. Equal parts of Isochemrez 444 and EM 207 (158-III) resulted in a flexible material of very low tensile strength, while a composition of 7 parts resin and 3 parts castor oil (158-IV) resulted in a rigid and brittle material. Reducing the amount of EM 207 in formulation 158-III, and increasing the amount of castor oil in formulation 158-IV may yield resins with suitable mechanical properties.

2. Fillers

The type of filler used in a particular resin system may greatly influence the performance of that material. However, to reduce the number of variables in the formulation of the insulation, only asbestos fillers are used routinely as reinforcement for the evaluation of resins in this program. For the better performing resins, the examination of other fillers is under way.

The use of potassium oxalate as a filler in the castor oil-modified Guardian formulations has been investigated. Because potassium oxalate settles out from the liquid resin, the viscosity was increased by partial curing before adding the oxalate. However, this technique was not successful because although the partially cured resin was quite viscous at room temperature and capable of holding the oxalate in suspension, on heating up to complete the cure, the system became quite fluid and allowed much of the potassium oxalate to settle out. The time interval between the highly viscous stage of the resin at the curing temperature and gelation is too short for practical use because the working time would be insufficient.

Cured material with oxalate uniformly distributed has been obtained by partially curing the resin and then adding, along with the oxalate, 10 per cent of asbestos powder. The asbestos powder gives sufficient body to the mixture to prevent the oxalate from settling out during the elevated temperature cure.

A 30- and a 40-per cent- castor oil-modified Guardian and an Epon 815-XR2000 (1:1 ratio) molding have been prepared containing 20 per cent of potassium oxalate and 10 per cent of asbestos powder. The Epon 815-XR2000 formulation containing 20 per cent of magnesium carbonate has also been molded. These materials were prepared by hand mixing and molded in a 6- by 3-inch mold or a 2-1/4-inch-diameter mold. Although these materials were prepared primarily to determine molding characteristics, they were also tested in the oxyacetylene torch (page 16). No difficulty was encountered in hand mixing and molding. The densities and molding conditions are reported in Table II. Also reported in Table II is a hand-mixed 40-per cent- castor oil-modified Guardian containing 20 per cent of asbestos fiber (3R100). The asbestos fiber and the resin are generally mixed in a sigma-blade mixer.

To determine the optimum amount of asbestos fiber for best insulation performance, 40-per cent-castor oil-modified Guardian formulations containing 13, 20, 30, 40, and 50 per cent of asbestos fiber were prepared for evaluation in static-motor tests (page 42). These moldings are described in Table II (Code numbers XXXII to XXXVI), and the relationship of density versus asbestos-fiber content is graphically shown in Figure 2.

3. Mechanical Testing

The effect of aging on the mechanical properties of unfilled, externally plasticized epoxy resins is being studied. Dumbbell specimens of unfilled Guardian, plasticized with dibutyl maleate or with Aroclor 1248, have been stored at ambient conditions and their mechanical properties and weight losses were determined at the end of 6 and 12 months. These results are summarized in Table III. Although these specimens are formulated to contain 50 per cent of plasticizer, some plasticizer is lost during the cure (1.75 hour at 125°C), especially with dibutyl maleate.

Table II
Preparation of Filled Epoxy Resins

| Specimen Number | Resin Composition ^a | Filler Composition | Molding Conditions | | Density (gm/cu cm) |
|-----------------|----------------------------------|--|--------------------|------------------|--------------------|
| | | | Pressure (psi) | Temperature (°F) | |
| XXX | 30%-castor oil-modified Guardian | 20% potassium oxalate ^b 10% asbestos powder ^c | 1,000 | 250 | 1.35 |
| XXXI | 40%-castor oil-modified Guardian | 20% potassium oxalate 10% asbestos powder | 1,000 | 250 | 1.32 |
| XXXIX | Epon 815/XR2000 (1:1 ratio) | 20% potassium oxalate 10% asbestos powder | 250 | 250 | 1.30 |
| XXXXI | Epon 815/XR2000 (1:1 ratio) | 22% magnesium carbonate ^d 0.8% carbon black ^e | 250 | 250 | 1.22 |
| XXXX | 40%-castor oil-modified Guardian | 21% asbestos fiber ^f | 250 | 250 | 1.29 |
| XXXII | 40%-castor oil-modified Guardian | 13% asbestos fiber | 1,000 | 325 | 1.22 |
| XXXIII | 40%-castor oil-modified Guardian | 20% asbestos fiber | 1,000 | 325 | 1.24 |
| XXXIV | 40%-castor oil-modified Guardian | 30% asbestos fiber | 1,000 | 325 | 1.33 |
| XXXV | 40%-castor oil-modified Guardian | 40% asbestos fiber | 1,000 | 325 | 1.45 |
| XXXVI | 40%-castor oil-modified Guardian | 50% asbestos fiber | 1,000 | 325 | 1.54 |

- a. Two per cent benzylidimethyl amine used as a catalyst. d. Fisher, U.S.P. powder.
b. Fisher Certified, $K_2C_2O_4 \cdot H_2O$. e. Added to color the material black.
c. Powhatan 7M. f. H. K. Porter, 3R100.

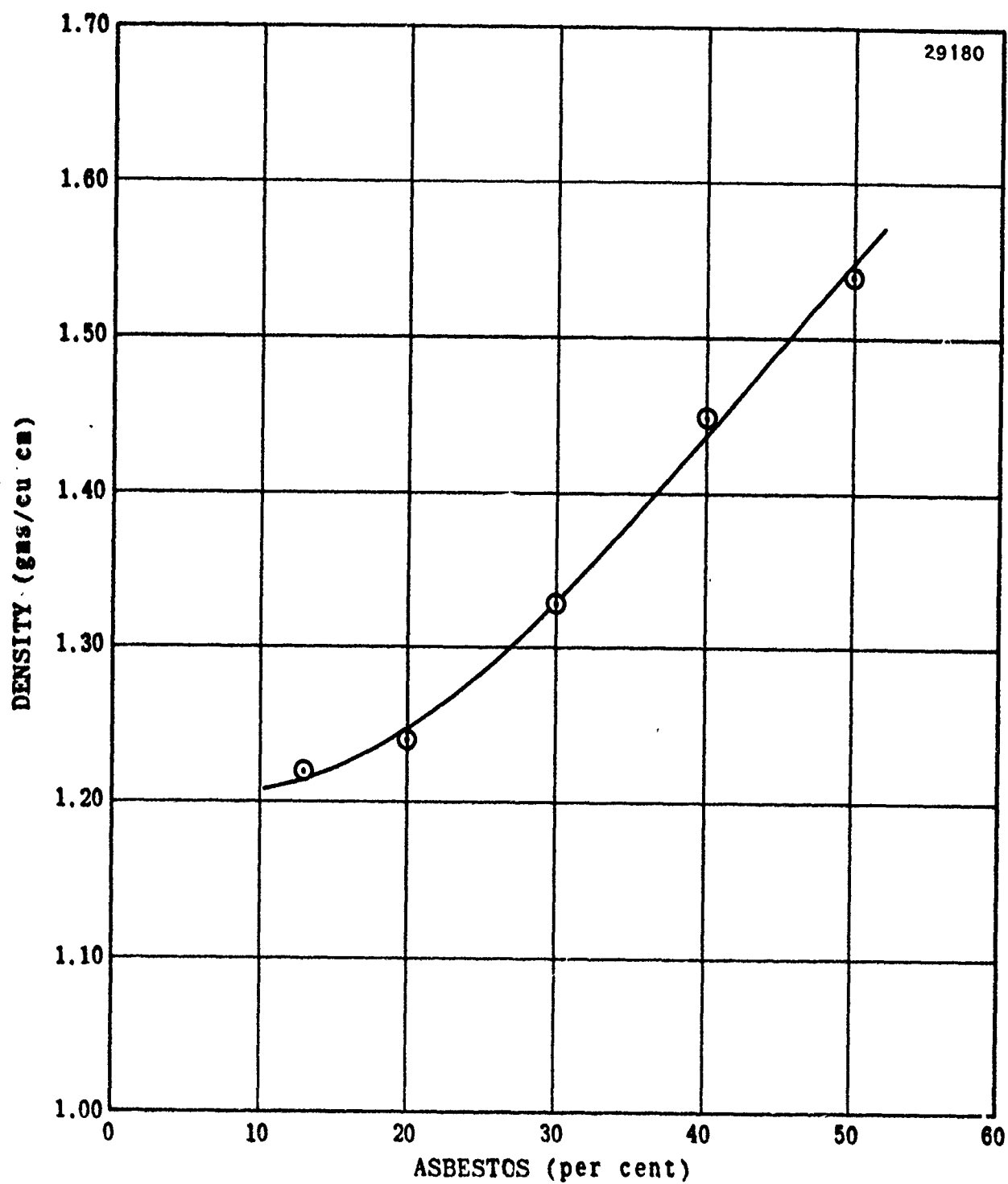


Figure 2. Relationship of Density and Asbestos Content for 40-Per Cent, Castor Oil Modified Guardian.

Table III

Aging Studies on Externally Plasticized Guardian

| Sample | Elongation ^a (per cent) | Tensile ^a Strength (psi) | Secant ^a Modulus (psi) | Weight Loss (per cent) |
|--|---------------------------------------|---|---|------------------------------|
| 50% Aroclor 1248 Plasticizer | | | | |
| <u>Initial</u> | | | | |
| A-1a | 90 | 1,160 | 1,290 | - |
| A-2a | 90 | 1,170 | 1,290 | - |
| A-3a | 97 | 1,260 | 1,310 | - |
| A-4a | 87 | 1,180 | 1,480 | - |
| Average | 91 | 1,292 | 1,342 | - |
| <u>6 Months</u> | | | | |
| A-5a | 57 | >2,000 ^b | - | 0.0 |
| A-1b | 59 | > 800 | - | 0.0 |
| A-2b | 53 | 1,760 | 3,460 | 0.0 |
| A-3b | 57 | 1,820 | 3,500 | 0.0 |
| Average | 57 | 1,790 | 3,480 | 0.0 |
| <u>12 Months</u> | | | | |
| A-4b | 40 | 1,028 | 2,056 | 0.5 |
| A-5b | 45 | 1,072 | 2,144 | 0.6 |
| A-1c | 55 | 987 | 1,974 | 0.5 |
| A-2c | 35 | 924 | 1,848 | 0.5 |
| Average | 44 | 1,003 | 2,005 | 0.5 |
| 50% Dibutyl Maleate Plasticizer | | | | |
| <u>Initial</u> | | | | |
| M-1a | 62 | 1,024 | 1,683 | - |
| M-2a | 62 | 1,082 | 1,718 | - |
| Average | 62 | 1,053 | 1,700 | - |
| <u>6 Months</u> | | | | |
| M-1b | 33 | > 400 | - | 8.0 |
| M-2b | Sample broke on handling | | | 10.4 |
| Average | 33 | > 400 | - | 9.2 |
| <u>12 Months</u> | | | | |
| M-1b | 15 | 814 | 1,628 | 12.2 |
| M-2c | 15 | 1,074 | 2,148 | 13.5 |
| Average | 15 | 944 | 1,888 | 12.9 |

a. Testing speed: 20 in/min; gage length: 2 inches.

b. Values marked > were obtained with the scale setting too low and as a result, only a minimum tensile strength was obtained and no secant modulus could be calculated.

By the end of 6 months, the dibutyl maleate dumbbell specimens had lost 9 per cent of their original weight and had bowed severely. At the end of 12 months the weight loss was 13 per cent and the elongation had decreased from 62 to 15 per cent. Dibutyl maleate is therefore unsuitable as a candidate plasticizer.

The Aroclor 1248-plasticized Guardian showed little or no weight loss over the 12-month period; however, the elongation decreased from 91 per cent to 57 per cent after 6 months, and to 44 per cent after 12 months. It is clear that the decrease in elongation cannot be attributed to the evaporation of the plasticizer. The decrease in elongation must arise because of further crosslinking of the resin through previously unreacted reactive sites. These reactive sites are present because they were separated from each other by the plasticizer during the initial cure. Because it is unlikely that this material would be sufficiently flexible for insulation application when filled with 40 per cent of asbestos fiber, it will not be further evaluated.

4. Oxyacetylene-Torch Testing

The oxyacetylene torch is convenient for screening insulation materials. Torch test conditions proposed by the Naval Ordnance Laboratory and standardized by a special committee on torch testing were used. The ratio of oxygen to acetylene was 1.2:1 at total flow rate of 225.0 std cu ft/hr. The spacing between the torch tip and specimen was 3/4 inch. Torch-test specimens are approximately 1/4-inch thick.

The time required for the backside of the specimens to reach 400°F is measured by a thermocouple. At 400°F the torch is turned off and the specimen is immediately flushed with nitrogen to prevent after-burning. Erosion is measured as the decrease in the sample thickness. Char penetration is determined by cutting the specimen in half and measuring the thickness of the remaining uncharred materials, and subtracting this value from the original thickness. In cases where the sample charred completely, only a minimum char rate can be calculated.

In Tables IV through VI are reported three series of torch-test results for asbestos-filled epoxy resins. Since changes are frequently made to improve the torch-test apparatus, torch data obtained with different modifications in the apparatus are not readily comparable, and, therefore, little attempt will be made to relate data of different tables.

Furthermore, since the torch test does not yield closely defined char and erosion rates, more emphasis should be placed on the temperature and weight-loss data.

The temperature index should be the most indicative parameter for relative insulation performance. On this basis, the three best materials in decreasing insulation performance in Table IV are (1) Epon 815 modified with XR2000 (1:1 ratio), (2) Guardian modified with 35 per cent of castor oil (varying Epon 828), and (3) Guardian plasticized with 30 per cent of dibutyl maleate. The over-all average ranking also rates these three materials as the best insulators of this group. The 40-per cent-castor oil-modified Guardian (varying NMA) is rated one of the poorest insulators in this group; however, previous torch and motor firing tests placed this material as one of the better insulators.

Of the materials reported in Table V, formulation IX-B and U. S. Rubber 3015 showed best insulation performance. This Oxiron 2000-Empol 1014 formulation (IX-B) is the first modified Oxiron to be tested in the oxyacetylene torch. Because of its good performance, other members of the Oxiron series, and their modifiers, should be tested. Many of these materials have already been shown to be very flexible, but in general they exhibited low tensile strength.

In the Tenth Monthly Progress Report (May 15, 1961), the preparation of 40-per cent-asbestos-filled, Guardian formulations in which the exposed faces would be protected by either two or three layers of Pluton* cloth was described. The oxyacetylene torch-test results of these materials are reported in Table V where formulation XI has two

* Minnesota Mining and Manufacturing Company

2. Preparation of Filled Melamine Resins

Attempts were made to prepare an asbestos-filled molding from the flexible diallyl melamine-QZ-8-0914 resin system. Equal parts of diallyl melamine and QZ-8-0914 were dissolved in warm acetone. The asbestos was added to this solution, and the acetone evaporated under vacuum at 50°C to give a material consisting of 60 per cent resin and 40 per cent asbestos fiber. Attempts to cure this material under conditions sufficient to cure the pure resin failed. Diallyl melamine is not very soluble in the QZ-8-0914 and will precipitate if the solution is not kept above 120°C. In the above case, when the acetone was evaporated, diallyl melamine undoubtedly precipitated on the asbestos, and then apparently, upon heating up during molding, it did not properly redissolve.

C. FLEXIBLE PHENOLIC RESINS

1. Determination of Physical Properties

Previously, A-stage phenol-formaldehyde resins which were modified for use as flexible insulators were prepared exclusively in the laboratory. However, because of practical and economic considerations involved in the production of prototype insulators, preliminary investigations were started during this period to evaluate a commercially available A-stage phenol-formaldehyde resin.

The first commercial resin evaluated was a Bakelite stage "A" phenol-formaldehyde resin, B2620. The mechanical properties of several B2620-Syl-Kem 90 formulations were determined. The results, shown in Table XIX, are compared with the mechanical properties of the standard phenolic resin also modified with Syl-Kem 90 and previously evaluated.

The tensile strengths of B2620-Syl-Kem 90 mixtures were relatively low and did not increase appreciably with resin concentration. However, the high tensile strengths of the standard phenolic-Syl-Kem 90 formulations changed rapidly with resin content. These results indicate that the B2620 has fewer available cross-link sites and that it probably has a higher molecular weight than the standard phenolic resin.

Table V

| Code Number | Formulation ^b | Cure Time (hr) | Cure Temperature (°F) | Asbestos Content (phr/100) | Density (g/cc) | Erosion Rate (mil/sec) | | | Char Rate (wt%/sec) | | | Temperature Index ^c (1,400°F, sec/in) | | | Weight Loss (per cent/sec) | | | Weight Loss (g/sec) | | | Over-All Average Rank |
|-------------|---|----------------|-----------------------|----------------------------|----------------|------------------------|---------|------|----------------------|---------|------|--|---------|------|----------------------------|---------|------|-------------------------|---------|------|-----------------------|
| | | | | | | Unit | Average | Rank | Unit | Average | Rank | Unit | Average | Rank | Unit | Average | Rank | Unit | Average | Rank | |
| Guardian | Epon 828 (10 parts) NMA (9 parts) | 1 | 250 | 40 | 1.55 | 4.36 | 4.36 | 5 | >7.63 | >7.63 | 5 | 122 | 122 | 5 | 1.372 | 1.312 | 8 | 0.281 | 0.281 | 7 | 6.2 |
| XI | 2 layers Pluton cloth on Guardian exposed surface | 2 | 250 | 44.6 ^d | 1.55 | 4.01 4.02 | 4.32 | 4 | 6.61 4.71 | 5.66 | 4 | 127 155 | 141 | 3 | 0.851 0.655 | 0.758 | 3 | 0.228 0.202 | 0.215 | 3 | 3.4 |
| XII | 2 layers Pluton cloth on Guardian exposed surface | 6.5 | 250 | 42.3 ^e | 1.51 | 3.56 4.32 | 3.94 | 3 | 5.56 4.92 | 5.04 | 3 | 127 125 | 126 | 4 | 1.028 0.958 | 0.958 | 4 | 0.262 0.233 | 0.258 | 5 | 3.8 |
| IX-B | Oxir in 2000/Epon 815 (1:1) | 3 | 250 | 40 | 1.28 | 3.17 3.08 | 3.12 | 2 | >5.21 >3.74 | >4.47 | 2 | 169 212 | 190 | 2 | 0.938 0.703 | 0.696 | 2 | 0.163 0.160 | 0.132 | 2 | 2.0 |
| SV-C | 20% castor oil-modified Guardian, varying Epon 828 | 2 | 325 | 40.1 | 1.46 | 4.76 3.87 | 4.32 | 4 | >8.71 5.32 | >7.01 | 5 | 109 135 | 22 | 5 | 1.092 0.922 | 1.007 | 5 | 0.263 0.231 | 0.237 | - | 4.6 |
| XVII2-C | Guardian with Epon 815 substituted for Epon 828 | 1 | 325 | 40.3 | 1.53 | 4.75 4.27 | 4.51 | 5 | >8.02 6.81 | >7.91 | 7 | 102 122 | 112 | 6 | 1.096 1.018 | 1.057 | 6 | 0.264 0.254 | 0.258 | 5 | 6.0 |
| XIX-B | 50% castor oil-modified Guardian, varying NMA and substituting Epon 815 for Epon 828 | 2.5 | 325 | 41.1 | 1.63 | >4.81 | >4.81 | 7 | >9.81 | >9.81 | 8 | 94.2 | 94.2 | 7 | 1.292 | 1.282 | 7 | 0.277 | 0.277 | 5 | 7.0 |
| XX-B | U S Rubber 3015 | - | - | - | 1.24 | 1.99 1.77 2.49 | 2.08 | 1 | 2.82 3.08 2.81 | 2.90 | 1 | 217 228 244 | 229 | 1 | 0.836 0.844 0.631 | 0.670 | 1 | 0.133 0.144 0.139 | 0.129 | 1 | 1.0 |

a Total burning time (used to calculate erosion, char, and weight loss rates) is generally not equal to time to 400°F but slightly longer
b (phr/100) is weight (lb) of filler (NMA) used as catalyst for curing the epoxy resin
c Temperature is defined as the ratio of the time required for the back of the sample to reach indicated temperature to the thickness of the specimen
d Basic methyl anhydride
e Per cent total filler (asbestos fiber and Pluton cloth)

Table VI

| Code Number | Formulation | Cure Conditions ^b | | Filler | Density (gm/cu. cm) | Specimen Thickness (in.) | Erosion Rate ^c (mil./sec) | | Char Rate ^d (mil./sec) | | Temperature Index ^e (1,000° F. sec/in) | | Weight Loss ^f (per cent/sec) | | Weight Loss ^g (gm/sec) | | Over-All Average Rank | | |
|-------------|--------------------------------|------------------------------|------------------|--|---------------------|--------------------------|--------------------------------------|-----------|-----------------------------------|--------------|---|----------------|---|----------------|-----------------------------------|----------------|-----------------------|---------|------|
| | | Time (hr) | Temperature (°F) | | | | Unit | Average | Rank | Unit | Average | Rank | Unit | Average | Rank | Unit | | Average | Rank |
| 41RPD | Rigid asbestos-phenolic resin | - | - | 75% asbestos | 1.50 | C 243 C 244 | 6.04 7.13 | 0.58 2 | - | - | 104.6 96.3 | 0.797 0.790 | 0.793 1 | 0.214 0.217 | 0.216 2 | 2.3 | 2.3 | | |
| VXXIX | Epon 815/H2000 (1.1) | 1 | 250 | 20% potassium oxalate 10% asbestos powder | 1.30 | 0.357 | 4.53 | 4.53 | 2 | 0.58 | 6.58 | 51.4 | 0.830 | 0.830 | 3 | 0.236 | 0.236 | 1 | 2.8 |
| VXX | 0L-Kastor oil-modified w ardan | 2 | 250 | 21% asbestos fiber | 1.29 | 0.303 0.301 | 2.49 2.11 | 2.30 | 1 | 7.66 4.07 | 5.87 | 139.7 155.9 | 0.856 0.780 | 0.918 | 2 | 0.212 0.190 | 0.201 | 1 | 1.2 |
| VXXI | Epon 815/H2000 (1.1) | 1 | 250 | 22% magnesium chloride 0.8% carbon black | 1.22 | 0.295 0.290 | 6.98 7.04 | 7.01 | 4 | 6.98 7.04 | 7.01 | 79.3 136.5 | 1.288 1.227 | 1.258 | 4 | 0.284 0.270 | 0.277 | 4 | 3.4 |

^a Torch test conditions are in accordance with the proposed standard of the Naval Ordnance Laboratory. ratio oxygen to acetylene 1.2:1, flow rate 225 std cu ft/hr. spacing between torch tip and specimen is 0.75 inch. At the end of testing, specimen is immediately flushed with nitrogen to prevent after-burning.

^b Pressure 250 psi

^c Erosion rate is the ratio of the decrease in specimen thickness to total burning time

^d Char is determined by cutting the specimen in half at the point of highest erosion and measuring the thickness of the remaining uncharred material, and subtracting the original thickness of the specimen from the remaining thickness.

^e Temperature index is defined as the ratio of the time required for the back side of the sample to reach 600°F to the thickness of the specimen

^f Per cent weight loss per second is defined as the ratio of the weight loss x 100 to the initial weight x total burning time.

^g Gram weight loss per second is defined as the ratio of the weight loss to the total burning time.

protective layers of Pluton cloth and formulation XII has three protective layers of Pluton cloth on the exposed face. The type of Pluton cloth used was the 8 oz/sq yd, single-ply, plain weave, staple fiber.

The data show that the Pluton cloth improves the insulation performance of the Guardian formulation. In most of the indexes, the improvement is only marginal, but there appears to be a substantial improvement in char rate.

Formulations XV-C, XVIII-C, and XIX-D exhibited very poor insulation performance in the torch test.

In Table VI are reported the oxyacetylene torch test results for some of the filled specimens described in Table II. Generally, torch-test specimens are 0.250-inch thick. However, these moldings were not actually prepared for this test and the variation in thickness from 0.243- to 0.357-inch adds to the difficulty in comparing their relative performance since the insulations parameters are somewhat affected by thickness. On the basis of the torch test, the potassium oxalate and the magnesium carbonate fillers do not appear to contribute as much to high insulation performance as the asbestos fiber does. However, preliminary data from motor firings indicate that a combination of asbestos fiber and one or these powder fillers gives materials with lower char rates.

5. Static-Motor Firing Tests

Insulation materials were tested at two positions in rocket motors: (1) along the motor case wall (peripheral slab), and (2) in the nozzle-approach (convergent) section of a motor using an end-burning grain. Service conditions are less severe in the peripheral slab test because of the lower gas velocity, less gas turbulence, and less particle impingement. Figure 3 shows these areas of thermal insulation in a rocket motor.

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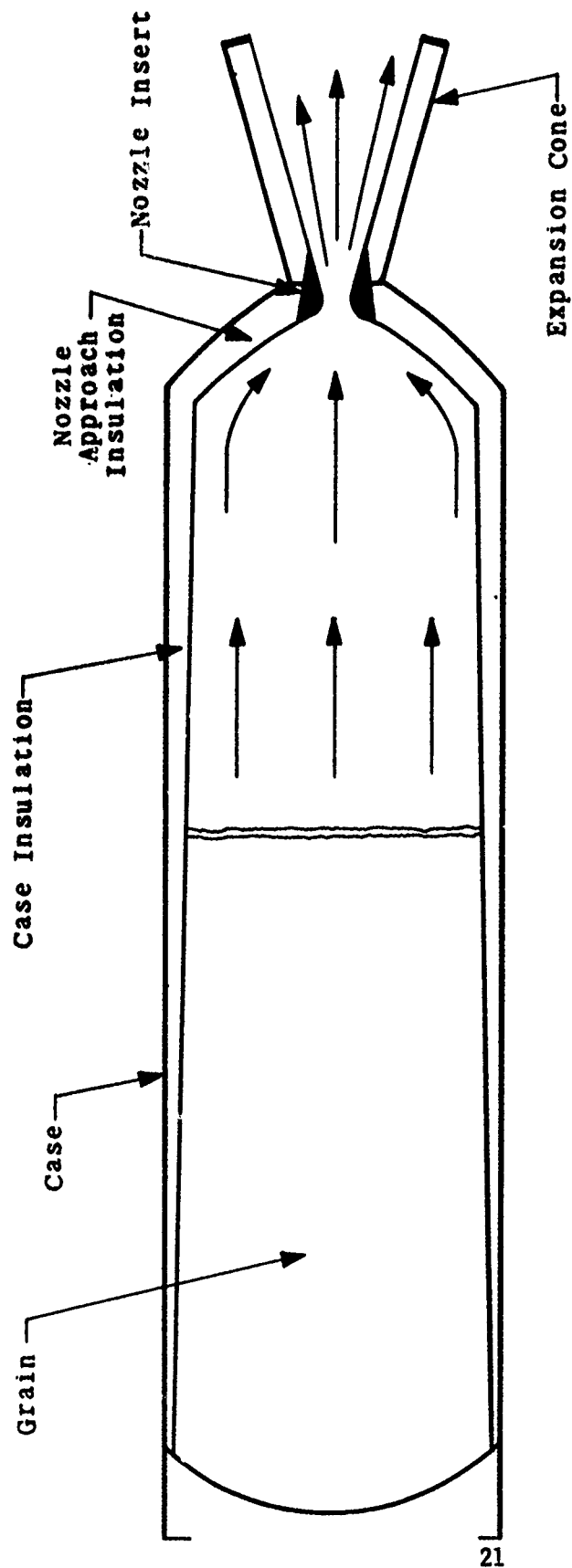


Figure 3. Cross Section of End-Burning Solid-Propellant Rocket Motor.

a. Convergent-Section Testing

The test specimens for convergent-section testing ($1\frac{3}{4}$ in \times $1\frac{1}{4}$ in \times $\frac{1}{2}$ -inch thick) are cut from the moldings. These specimens are then mounted around the face of the convergent section of an end-burning motor and held in place by embedding with an epoxy-asbestos material. Such a mounting allows only the flat-front surface of the specimen to be exposed to the hot combustion gases. The nozzle-approach section before and after the motor has been fired is shown in Figures 4 and 5. The outline of the six tested specimens in Figure 5 can be seen at the 2-, 4-, 6-, 8-, 10-, and 12-o'clock positions. The char penetration is determined by cutting the specimen, measuring the thickness of the uncharred material, and subtracting this value from the original thickness of the specimen. The char rate is calculated as the ratio of the decrease in thickness of the uncharred material to the total firing time of the motor.

In Tables VII through XI are reported the results of several convergent-motor firings. Tested materials from motor firings M-298, M-300, and PYB-8 are shown in Figures 6, 7, and 8.

b. Peripheral-Slab-Section Testing

For peripheral-slab-section testing, eight test specimens ($3\text{-} \times 2\text{-} \times \frac{1}{2}$ -inch thick) are mounted around the inside face of a phenolic-octahedral cylinder with Armstrong's A-2 adhesive as shown in Figure 9. The cylinder is then positioned in the rocket motor so that the hot propellant gases flow parallel to the face of each test specimen. After the motor is fired, the specimens are cut in half and char penetration and char rate are calculated as described above for convergent-section testing. In Tables XII through XV are reported the results of several peripheral-slab motor firings. Tested specimens from the motor firings are shown in Figures 10, 11, 12, and 13.

Although motor firing B-68 had a failure, the specimens in that motor can be compared with each other and their relative performance compared to the performance of identical materials in the successful convergent-motor firing M-298 (Table IX).

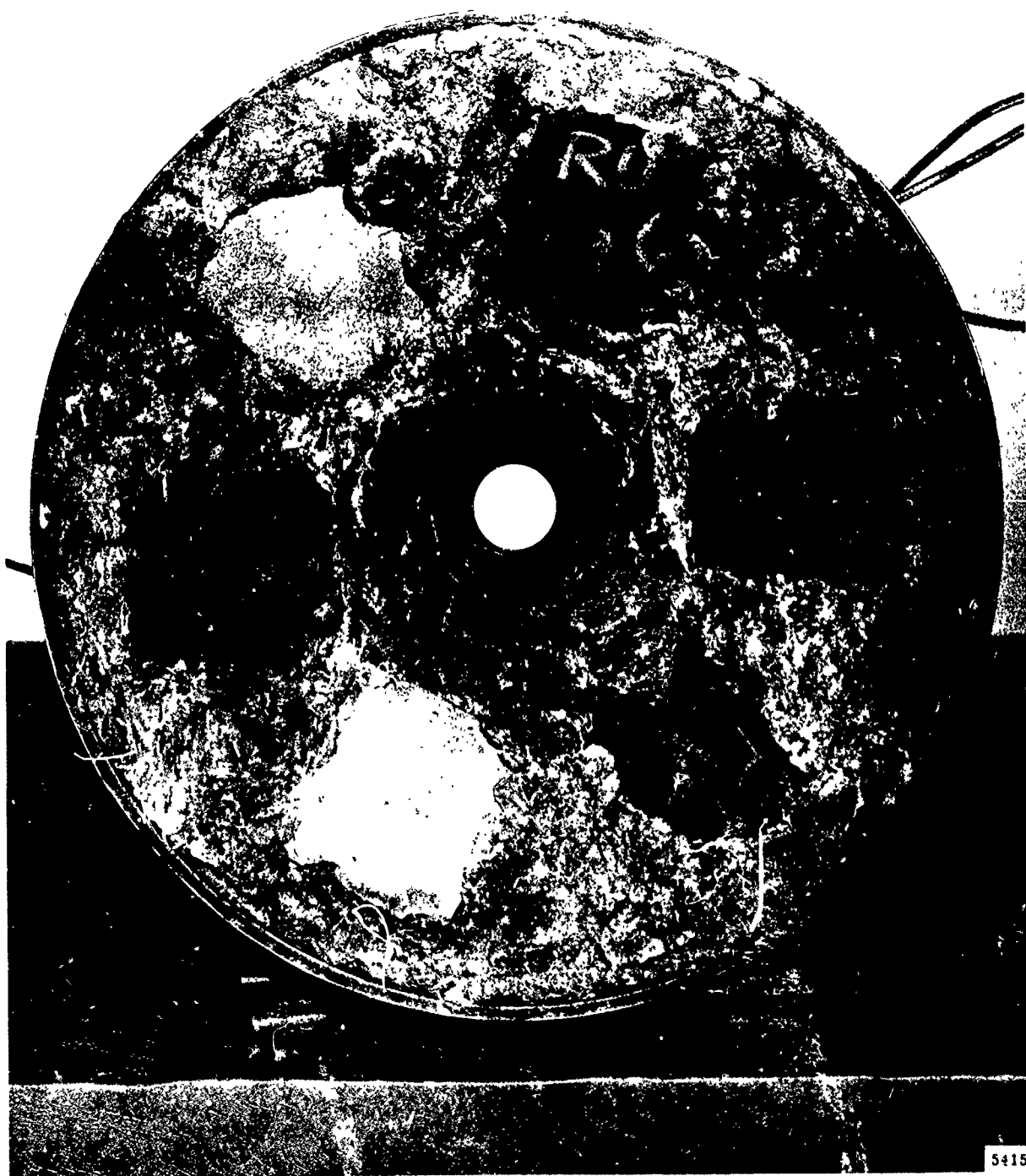


Figure 4. Test Specimens in the Convergent Section Before Motor Firing.

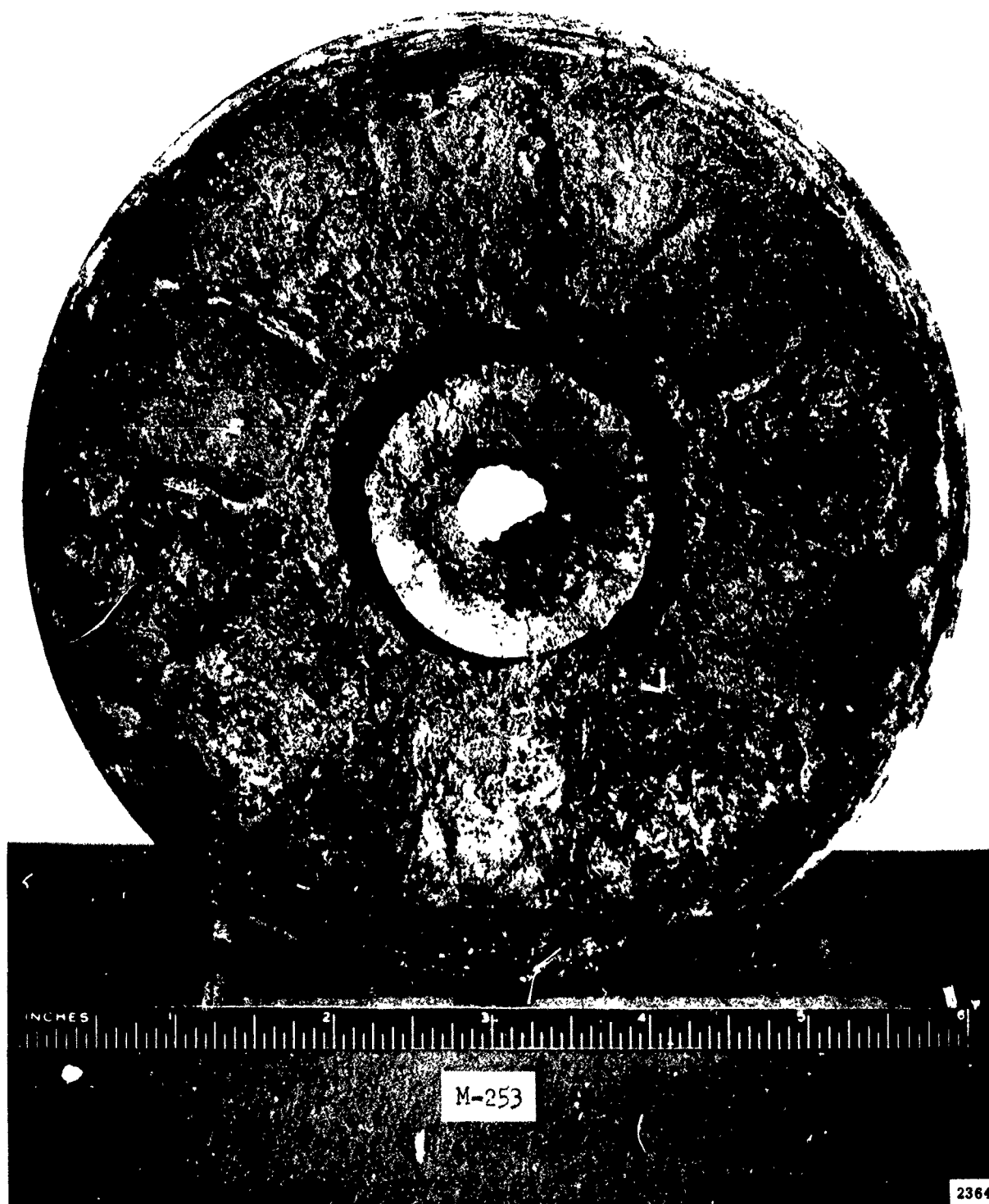


Figure 5. Test Specimens in the Convergent
Section After Motor Firing.

Table VII
Convergent-Section Motor Firing M-275 Results for Filled Epoxy Resins^a

| Code Number | Formulation (parts) | Density (gm/cu cm) | Cure Conditions | | Asbestos (3R100) Content (per cent) | Char Rate (mil/sec) | Char Rate Specimen/Char Rate Guardian ^b and Rank | | Char Rate X Density |
|-------------|---|--------------------|------------------|--------------|-------------------------------------|---------------------|---|--|---------------------|
| | | | Temperature (°F) | Time (hr) | | | | | |
| VIII-B | Araldite DP-437 (10) Ciba Hardner 951 (1) | 1.44 | 250 | 0.75 | 40 | 3.7 | 0.77 (2) | | 5.3 |
| IV | Epon 815 (1) XR2000 (1) BDMA (2.5 per cent) | 1.40 | 140 250 | 0.75 0.75 | 42 | 3.4 | 0.71 (1) | | 4.8 |
| III | Epon 828 (10) NMA (5) BDMA (2.5 per cent of above) DBM ^c (8.36) (30 per cent) | 1.56 | 250 | 2.25 | 47 | 4.3 | 0.90 (3) | | 6.7 |
| II | Epon 828 (10) NMA (9) BDMA (2.5 per cent of above) Aroclor 1248 (19) (50 per cent) | 1.64 | 250 | 2.75 | 43 | 4.6 | 0.96 (4) | | 7.5 |
| Guardian | Epon 828 (10) ^d NMA (9) BDMA (2.5 per cent of above) | 1.55 | 250 | 2.0 | 40 | 4.8 | 1.00 (5) | | 7.5 |

- a. Length of firing: 43.7 sec; flame temperature: 5600°F; high pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
b. Specimens ranked in decreasing effectiveness from 1 to 5.
c. DBM-Dibutyl maleate.
d. Used as a comparative standard.

Table VIII

Convergent-Section Motor Firing B-16 Results for Filled Epoxy Resins^a

| Code Number | Formulation | Density (gm/cu cm) | Cure Conditions | | Asbestos (3R100) Content (per cent) | Char Rate (mil/sec) | Char Rate Specimen/Char Rate Guardian ^b and Rank ^b | | Char Rate X Density |
|------------------------------|--|--------------------|------------------|-----------|-------------------------------------|---------------------|--|-----|---------------------|
| | | | Temperature (°F) | Time (hr) | | | | | |
| XVII-D | 35%-castor oil-modified Guardian, varying Epon 828 | 1.42 | 325 | 2.0 | 40 | 3.9 | 0.76 (4) | 5.5 | |
| | | | | | | | | | |
| XIX-D | 30%-castor oil-modified Guardian, varying NMA and replacing Epon 828 by Epon 815 | 1.43 | 325 | 2.5 | 41 | 3.4 | 0.67 (3) | 4.9 | |
| | | | | | | | | | |
| XIV-F | 40%-castor oil-modified Guardian, varying NMA | 1.41 | 325 | 2.5 | 41 | 3.0 | 0.59 (1) | 4.2 | |
| | | | | | | | | | |
| Guardian Epon 828 (10 parts) | NMA (9 parts) BDMA (2.5 per cent of above) | 1.55 | 250 | 2.0 | 40 | 5.1 | 1.00 (5) | 7.9 | |
| | | | | | | | | | |
| Ru 146 | U.S. Rubber 3015 ^c | 1.24 | --- | --- | -- | 3.2 | 0.63 (2) | 4.0 | |

- a. Length of firing: 43.6 sec; flame temperature: 6500°F; high pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
- b. Specimens ranked in decreasing effectiveness from 1 to 5.
- c. Included in firing as a comparative standard.

Table IX
Convergent-Section Motor Firing M-298 Results for Filled Epoxy Resins^a

| Code Number | Formulation (parts) ^b | Density (gm/cu cm) | Asbestos Fiber Content (per cent) | Char Rate (mil/sec) | Char Rate X Density |
|----------------|--|-----------------------|---|---------------------------|---------------------|
| XXXII-B | 40%-castor oil- modified Guardian, varying NMA | 1.22 | 13 | 2.5 | 3.0 |
| XXXIII-A | 40%-castor oil- modified Guardian, varying NMA | 1.24 | 20 | 1.6 | 2.0 |
| XXXIV-A | 40%-castor oil- modified Guardian, varying NMA | 1.33 | 30 | 2.6 | 3.5 |
| XXXV-A | 40%-castor oil- modified Guardian, varying NMA | 1.45 | 40 | 1.9 | 2.8 |
| XXXVI-A | 40%-castor oil- modified Guardian, varying NMA | 1.54 | 50 | 1.9 | 2.9 |
| Ru 86 | Gen-Gard V-44 ^c (asbestos-filled rubber, NBR) | 1.28 | --- | --- | --- |

- a. Length of firing: 92.4 sec; flame temperature 5600°F; medium pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
b. Epoxy resins cured at 325°F for 2 hours.
c. Included in firing as a comparative standard. One of the best commercially available materials.
d. Alteration of material too extensive to calculate quantitative char rate.

TABLE X

Convergent-Section Motor Firing M-300 Results for Filled Epoxy Resins^a

| Code Number | Formulation (parts) | Density (gm/cu cm) | Cure Conditions | | Asbestos Fiber Content (per cent) | Char Rate (mil/sec) | Char Rate x Density |
|----------------|--|-----------------------|---------------------|--------------|---|---------------------------|---------------------|
| | | | Temperature (°F) | Time (hr) | | | |
| X-B | Araldite DP-437/ NMA ^L (1:1) | 1.52 | 250 | 2 | 40 | 2.4 | 3.6 |
| Ru 146 | U. S. Rubber Company's 3015 ^C | 1.24 | --- | --- | potassium oxalate filler | 2.6 ^d | 2.1 |

- Length of firing: 66.1 sec; flame temperature: 5600°F; medium pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
- 2.5 per cent DBMA used as catalyst.
- Included in firing as a comparative standard. One of the best commercially available materials.
- Some swelling and voids in uncharred material.

Table XI
Convergent-Section Motor Firing PYB-8 Results for Filled Epoxy Resins^a

| Code Number | Formulation ^b (parts) | Cure Conditions | | Filler Content (per cent) | Char Rate (mil/sec) | Char Rate × Density |
|----------------|---|---------------------|--------------|--|---------------------------|------------------------|
| | | Temperature (°F) | Time (hr) | | | |
| Guardian | Epon 828-NMA (10:9) ^c | 250 | 2 | 40% asbestos fiber (3R100) | 4.9 | 7.6 |
| EA8 83 | Epon 828-NMA (10:9) ^c | 250 | 2 | 60% asbestos fiber (3R100) | 4.0 | --- |
| XXXI | 40%-castor oil- modified Guardian, varying NMA | 250 | 3 | 20% potassium oxalated 10% asbestos powdere | 1.1 ^f | 1.3 |

- a. Length of firing: 34.8 sec; flame temperature: 6500°F; medium pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
- b. 2.5 per cent BDMA used as catalyst.
- c. Rigid materials.
- d. Fisher certified, $K_2C_2O_4 \cdot H_2O$.
- e. Powhatan 7M.
- f. Resin altered throughout uncharred material and extensive swelling prevents calculation of a realistic char rate.

29184

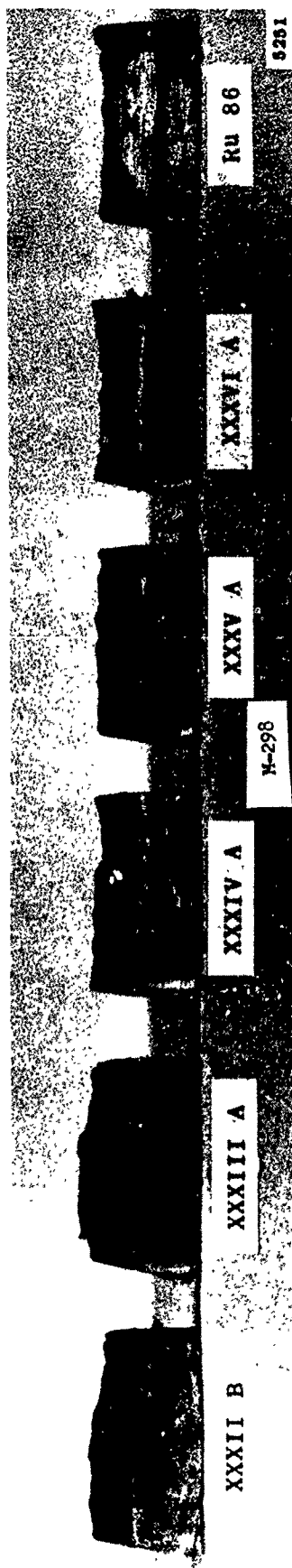


Figure 6.



Figure 7.

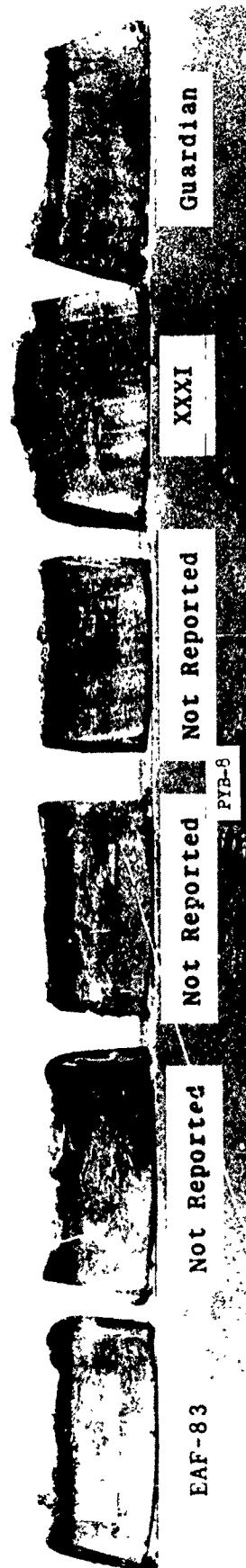


Figure 8.

Figures 6, 7, 8. Convergent-Section Test Specimens from Firings M-298, M-30, and PYB-8.

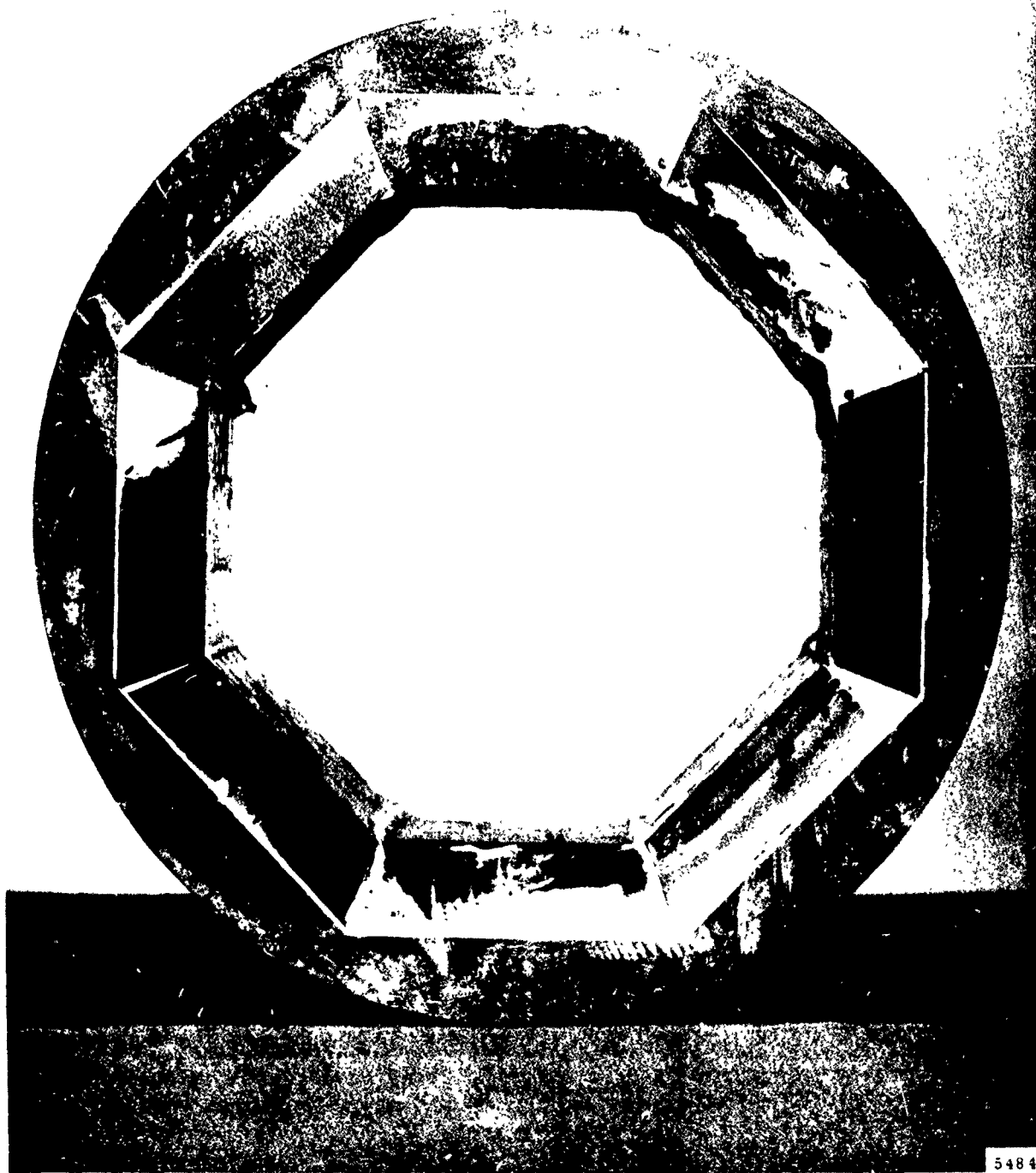


Figure 9. Test Specimen in the Peripheral-Slab
Section Before Motor Firing.

Table XII

Peripheral-Slab Motor Firing PYM-3 Results for Filled Epoxy Resins^a

| Code Number | Formulation (parts) | Asbestos (3R100) Content (per cent) | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate Specimen/ Char Rate of Guardian | Char Rate × Density |
|----------------|--|---|-----------------------|------------------------|--|------------------------|
| Guardian | Epon 828 (10) NMA (9) | 40 | 1.55 | 4.1 | 1.00 | 6.3 |
| IV-A | Epon 815 (1) XR2000 (1) BDMA (2.5 per cent) | 40 | 1.40 | 3.3 | 0.80 | 4.6 |
| 3-A | Epon 828 (1) Thiokol EM206 (1) BDMA (2.5 per cent) | 40 | 1.51 | 3.2 | 0.78 | 4.8 |
| V-A | 30%-castor oil- modified Guardian, varying NMA | 41 | 1.47 | 2.2 | 0.54 | 3.2 |
| Ru 146 | U. S. Rubber Insulation 3015 ^b | potassium oxalate | 1.24 | 3.0 | 0.73 | 3.7 |

a. Length of firing: 63.5 sec; flame temperature: 5600°F; high pressure; motor quenched with nitrogen at the end of firing to prevent after-burning of the specimen.

b. Included in firing as a comparative standard.

Table XIII

Peripheral-Slab Motor Firing M-284 Results of Filled Epoxy Resins^a

| Code Number | Formulation (parts) | Asbestos (3R100) Fiber (per cent) | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate | |
|----------------|--|---|-----------------------|------------------------|------------------------------------|------------------------|
| | | | | | Specimen/ Char Rate Guardian | Char Rate × Density |
| VIII-A | Araldite DP-437 ^b | 40.0 | 1.44 | 3.2 | 0.91 | 4.6 |
| X-A | Araldite DP-437 ^c (10) NMA (9) | 40.3 | 1.52 | 2.4 | 0.69 | 3.6 |
| XVIII-A | Epon 815 ^c (10) NMA (9) | 40.3 | 1.53 | 3.5 | 1.00 | 5.4 |
| Guardian | Epon 828 ^c (10) NMA (9) | 40.0 | 1.54 | 3.5 | 1.00 | 5.4 |
| Ru 146 | U. S. Rubber Insulation 3015 ^d | --- | 1.24 | 2.7 | 0.77 | 3.3 |
| 41RPD | Asbestos-phenolic ^d | 70 to 75 | 1.5 | 2.7 | 0.77 | 4.0 |

a. Length of firing: 62.3 sec; flame temperature: 5600°F; high pressure; quenched with nitrogen at end of firing to prevent after-burning of specimens.

b. Cured with 10 per cent Hardner 951.

c. 2.5 per cent benzyl dimethyl amine used as a catalyst.

d. Included in firing as a good, commercially available insulation.

Table XIV

Peripheral-Slab Motor Firing B-35 Results for Filled Epoxy Resins^a

| Code Number | Formulation | Asbestos (3R100) Fiber (per cent) | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate × Density |
|-------------|--|-----------------------------------|--------------------|---------------------|---------------------|
| XXVII-A | 30%-LP-8-modified Guardian ^b (ratio of Epon 828:NMA:LP-8 is 1.07:1.26:1.00) | 40.4 | 1.56 | 4.1 ^f | 6.4 |
| XXV-A | 1 part Epon 828 - 1 part EM 207 ^b | 40.2 | 1.50 | 4.1 | 6.1 |
| XXIII-A | 30%-castor oil- ^b modified Guardian ^h | 40.3 | 1.45 | 4.3 ^f | 6.2 |
| XXVI-A | 30%-castor oil- ^{b,c} modified Guardian | 40.1 | 1.46 | 4.5 ^f | 6.6 |
| V-B | 30%-castor oil- ^{b,d} modified Guardian | 42.8 | 1.46 | 3.9 | 5.7 |
| Ru 146 | U. S. Rubber 3015 ^e | --- | 1.24 | 3.2 | 4.0 |
| 41RPD | Asbestos-phenolic ^e | 70 to 75 | 1.50 | 5.0 | 7.5 |

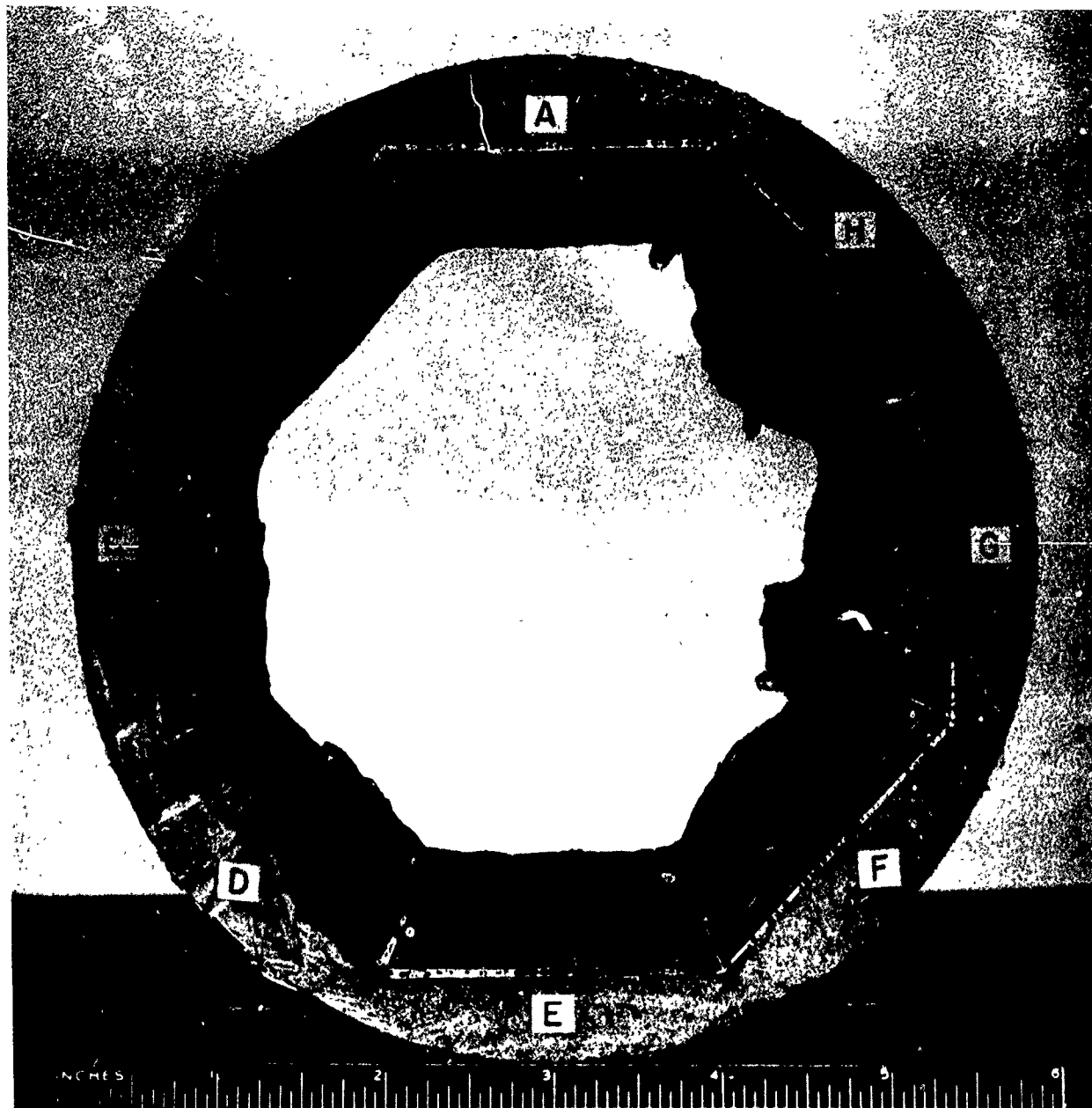
- a. Length of firing: 46.3 sec; flame temperature: 6500°F; high pressure; quenched with nitrogen at end of firing to prevent after-burning of specimens.
b. 2.5 per cent benzyl dimethyl amine used as a catalyst.
c. Differs from formulation XXIII-A and V-B in that the castor oil and NMA were pre-cooked at 150°C for 3 hrs before mixing in epoxy resin.
d. Like formulation XXIII-A. One of the earlier preparations.
e. Include in firing as a good, commercially available insulation.
f. These char rates were incorrectly reported in a previous Quarterly Progress Report (January, 1962).

Table XV

Peripheral-Slab Motor Firing B-68 Results for Filled Epoxy Resins^a

| Code Number | Formulation | Asbestos Fiber (3R100) Content (per cent) | Density (gm/cu cm) | Char Penetration, mil ^b (Char Rate, mil/sec) ^c | Char Rate × Density |
|-------------|---|---|--------------------|---|------------------------|
| XXXII-B | 40%-castor oil-modified Guardian, varying NMA | 13 | 1.22 | 19 (2.5) | 3.0 |
| XXXIII-A | 40%-castor oil-modified Guardian, varying NMA | 20 | 1.24 | 18 (2.4) | 3.0 |
| XXXIV-A | 40%-castor oil-modified Guardian, varying NMA | 30 | 1.33 | 19 (2.5) | 3.3 |
| XXXV-A | 40%-castor oil-modified Guardian, varying NMA | 40 | 1.45 | 13 (1.7) | 2.5 |
| XXXVI-A | 40%-castor oil-modified Guardian, varying NMA | 50 | 1.54 | 13 (1.7) | 2.6 |
| Ru 86 | Gen-Gard V-44 ^d (asbestos-filled rubber, NBR) | --- | 1.28 | 16 (2.1) | 2.7 |

- a. Motor was not a successful firing. Burned out through the side above the samples. A 6500°F propellant was used which burned for 3 or 4 minutes at ambient pressure.
- b. Although the firing was a failure, the specimens were exposed to identical environment and a relative comparison can be made on the basis of char penetration. Char penetration is calculated by subtracting the thickness of the uncharred material from the original thickness of the specimen.
- c. A relative char rate for these materials is calculated by assuming the char rate for molding XXXII-B to be 2.5 mil/sec (this is the value obtained for this material in motor firing M-298, Table IX) and adjusting the values for the other specimens proportionally.
- d. Included in firing as a comparative standard.

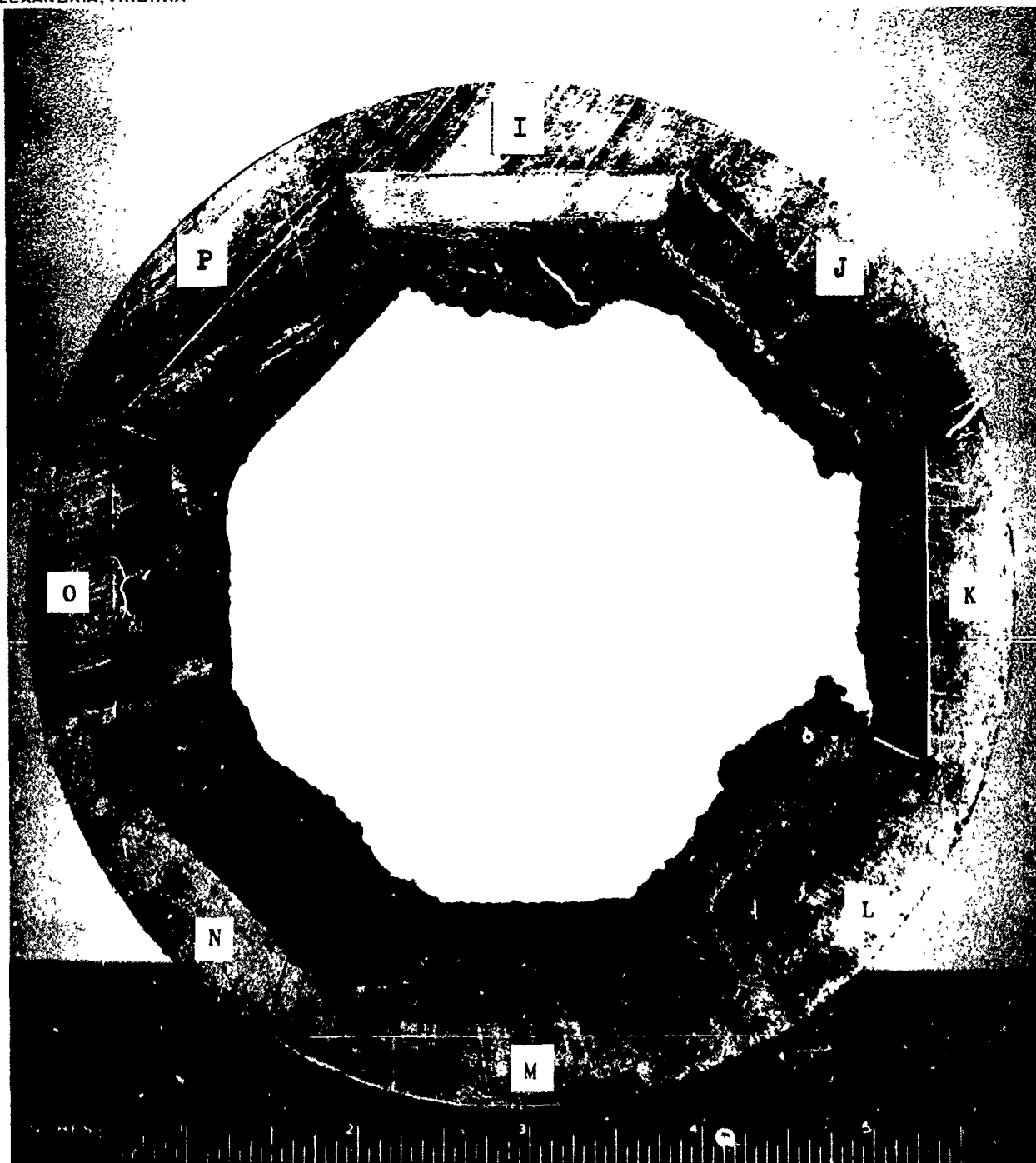


PYM-3

A - Guardian
B - IV a
C - 3 a
D - Not Reported

E - V a
F - Not Reported
G - Not Reported
H - Ru 146

Figure 10. Peripheral-Slab Test Specimens
from Firing PYM-3.



M-284

I - Not Reported
J - Not Reported
K - Ru 146
L - Not Reported

M - VIII A
N - X A
O - XVIII A
P - Guardian

Figure 11. Peripheral-Slab Test Specimens
from Firing M-284.

29188

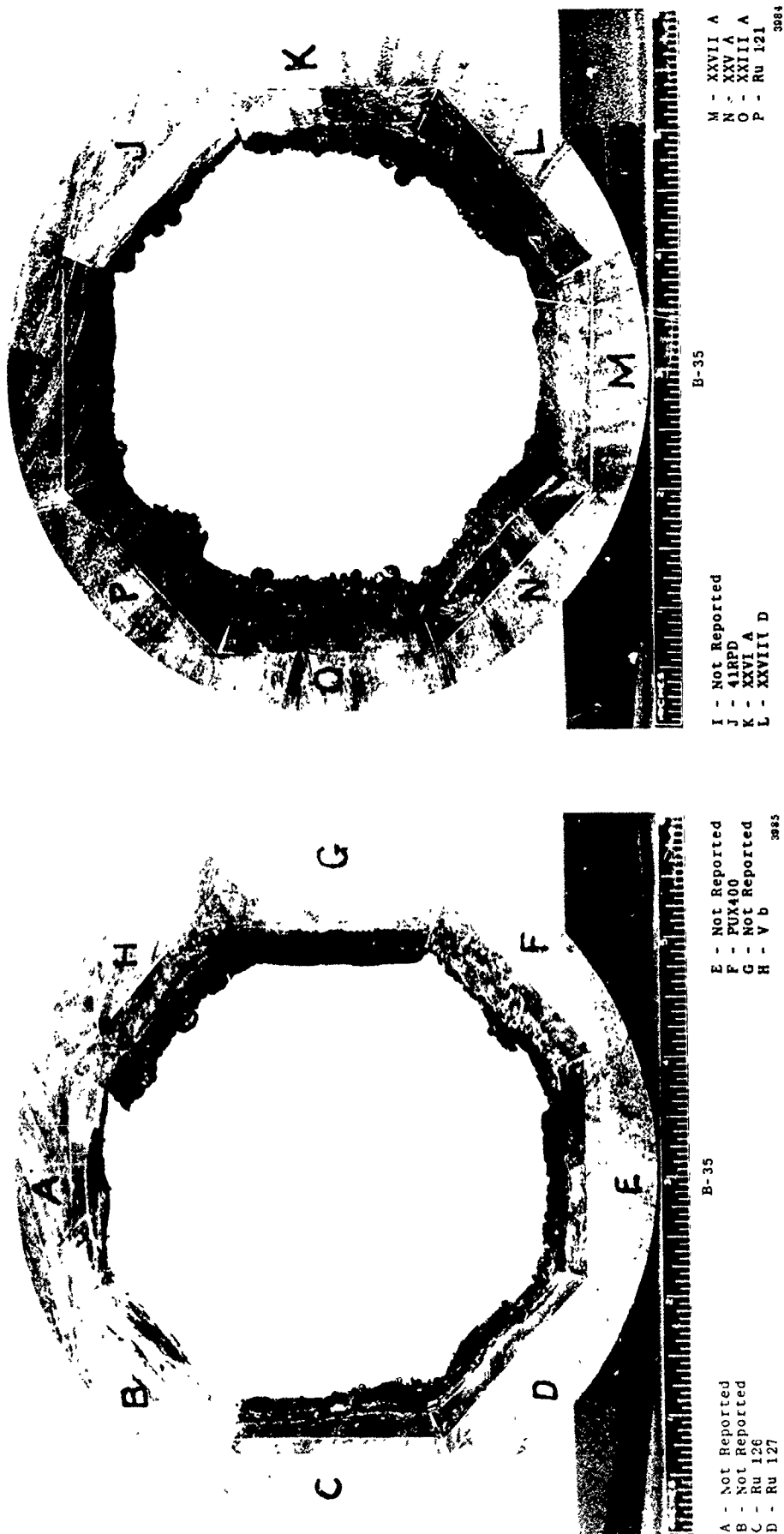
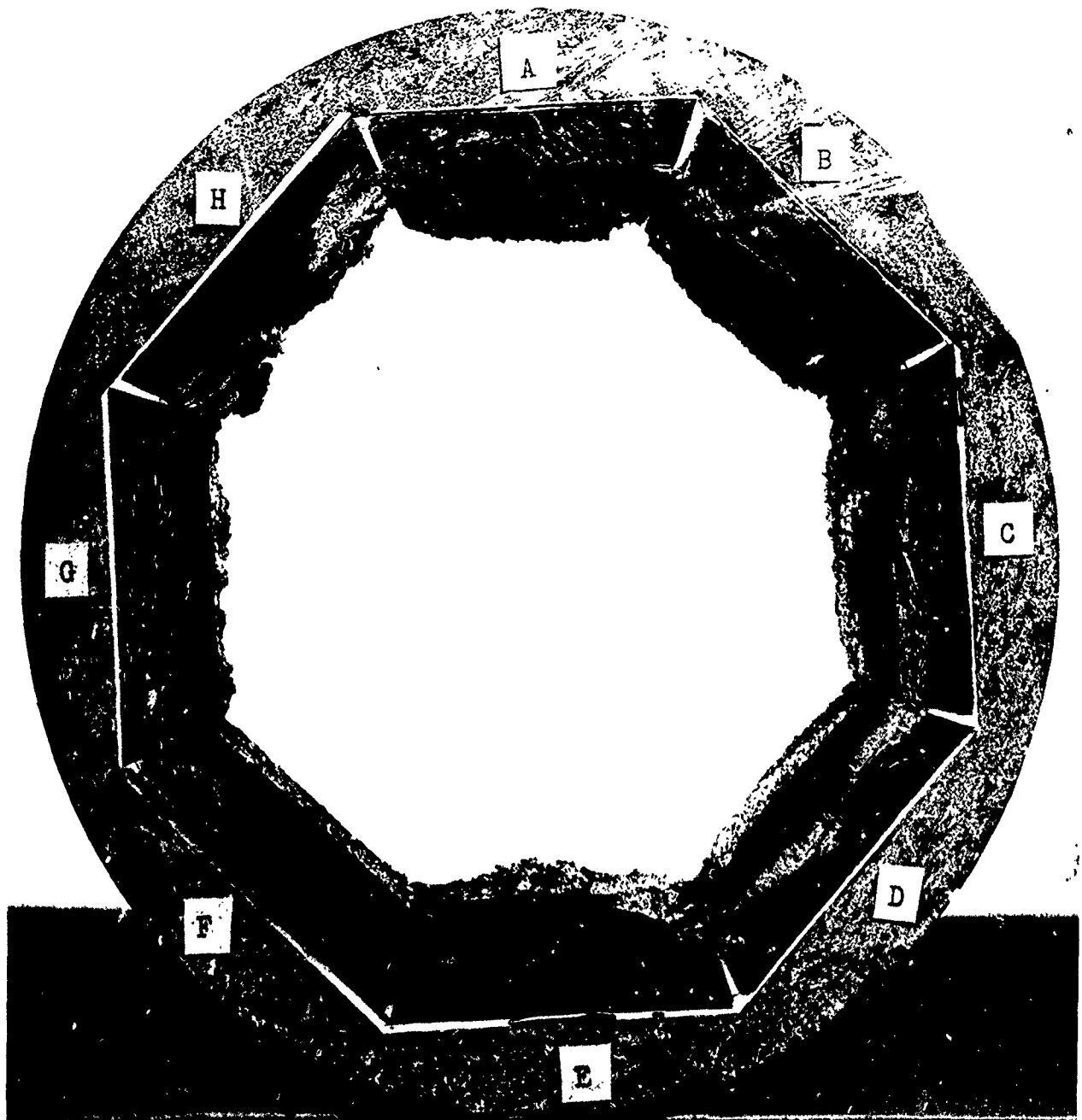


Figure 12. Peripheral-Slab Test Specimens from Firing B-35.



B-68

A - XXXII
B - XXXIII
C - XXXIV
D - XXXV

E - XXXVI
F - Not Reported
G - Not Reported
H - Ru 86

5327

Figure 13. Peripheral-Slab Test Specimens
from Firing B-68.

c. Discussion of Motor-Firing Tests

In evaluating the performance of an insulator, the product of char rate and density represents the relative weight of material needed for a given insulation requirement. The material with the lowest char rate-density number would therefore be the most effective material if one assumes that the volume requirements of the various insulating materials can be ignored. This assumption would generally be valid considering the energy of present-day propellants and the small difference in volume requirements of most of the candidate insulations.

(1) Optimum Asbestos-Fiber Loadings

From firings M-298 (Table IX) and B-68 (Table XV), the optimum loading for maximum insulation performance (based on both char rate and density) is 40 per cent of asbestos fiber and 60 per cent of resin for the 40-per cent-castor oil-modified Guardian formulation. The product of char rate and density for this flexible material is 2.5, while the value for one of the best commercially available insulators is 2.7 mil-gm/sec-cu cm (Table XV). The low char rate for XXXIII-A in Table IX is probably in error, as indicated by the data in Table XV; however, this material is being re-tested.

The low char rates for the materials in motor firing M-298 (Table IX) result from the long firing time of 92.4 sec. Generally, char rates decrease as the firing time increases. This is why one must proceed with caution in comparing materials in different motor firings and why a comparative standard is generally included in each firing.

(2) Modifications of Guardian

The motor firing results for the various 40-per cent-asbestos-fiber-filled Guardian modifications are summarized in Table XVI. U. S. Rubber 3015 was used as a comparative standard. By dividing the char rates by the char rate of 3015 in the same motor firing, comparisons can be made from motor to motor. The following conclusions are based on the data in Table XVI.

Table XVI
Comparison of Char Rates of Guardian Modifications Containing 40 Per Cent Asbestos Fiber

| Code Number | Formulation | Density (gm/cu cm) | Motor Firing Number and Table Reported | Type of Firing (Slab or Convergent) | Propellant Temperature (°F) | Firing Time (sec) | Pressure | Char Rate (mil./sec) | Char Rate U. S. Rubber 3015 in Same Motor Firing |
|-------------|--|--------------------|--|-------------------------------------|-----------------------------|-------------------|----------|----------------------|--|
| XVII-D | 35%-castor oil-modified Guardian, varying Epon 828 | 1.42 | B-16 (VIII) | convergent | 6500 | 43.6 | high | 3.9 | 1.22 |
| XIX-D | 30%-castor oil-modified Guardian, varying NMA and replacing Epon 828 by Epon 815 | 1.43 | B-16 (VIII) | convergent | 6500 | 43.6 | high | 3.4 | 1.06 |
| XIV-F | 40%-castor oil-modified Guardian, varying NMA | 1.41 | B-16 (VIII) | convergent | 6500 | 43.6 | high | 3.0 | 0.94 |
| Guardian | Guardian | 1.55 | B-16 (VIII) | convergent | 6500 | 43.6 | high | 5.1 | 1.59 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | B-16 (VIII) | convergent | 6500 | 43.6 | high | 3.2 | 1.00 |
| XVIII-A | Replacing Epon 815 for Epon 828 in Guardian | 1.53 | M-284 (XIII) | peripheral | 5600 | 62.3 | high | 3.5 | 1.29 |
| Guardian | Guardian | 1.54 | M-284 (XIII) | peripheral | 5600 | 62.3 | high | 3.5 | 1.29 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | M-284 (XIII) | peripheral | 5600 | 62.3 | high | 2.7 | 1.00 |
| V-A | 30%-castor oil-modified Guardian, varying NMA | 1.47 | PYM-3 (XII) | peripheral | 5600 | 63.5 | high | 2.2 | 0.73 |
| Guardian | Guardian | 1.55 | PYM-3 (XII) | peripheral | 5600 | 63.5 | high | 4.1 | 1.37 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | PYM-3 (XII) | peripheral | 5600 | 63.5 | high | 3.0 | 1.00 |
| XXIII-A | 30%-castor oil-modified Guardian, varying NMA | 1.45 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 4.3 | 1.34 |
| XXVI-A | 30%-castor oil-modified Guardian, varying NMA | 1.46 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 4.5 | 1.40 |
| V-B | 30%-castor oil-modified Guardian, varying NMA | 1.46 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 3.9 | 1.22 |
| XXVII-A | 30% LP-8-modified Guardian | 1.56 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 4.1 | 1.28 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 3.2 | 1.00 |

- (a) The material having the best comparative char rate is the 40-per cent-castor oil modification (number XIV-F). Although the 30-per cent-castor oil modification showed a lower char rate in one example (V-A), other examples show the 30- and 35-per cent-castor oil modifications should be ranked lower (XVII-D, XXIII-A, XXVI-A, V-B).
- (b) The comparative char rates indicate that the substitution of Epon 815 for Epon 828 may have some beneficial effect (compare XIX-D versus XXIII-A, XXVI-A, and V-B); and, at worst, no harmful effect (compare XVIII-A with the Guardian directly below it).
- (c) When more Epon 828 instead of NMA was added to react with the added castor oil* in the modified Guardian formulation, insulator effectiveness apparently was not affected (compare XVII-D, XXIII-A, and XIV-F); from previous testing, the char rate would be expected to decrease as the concentration of castor oil increased.
- (d) The use of Thiokol LP-8 in place of castor oil to flexibilize the Guardian formulation resulted in a material of approximately the same performance (see XXVII-A).

(3) New Flexible Epoxy Resins

The motor firing results for new flexible epoxy resins containing 40 per cent of asbestos fiber are summarized in Table XVII. U. S. Rubber 3015 was used on a comparative standard (except for the first motor firing, M-275). By dividing the char rates by the char rate of 3015 in the same motor firing, comparisons can be made from motor to motor (except for M-275). The following conclusions are based on the data in Table XVII.

* This point is discussed on page 6.

Table XVII
Comparison of Char Rates of New Flexible Epoxy Resins Containing 40 Per Cent Asbestos Fiber

| Code Number | Formulation (parts) | Density (gm/cu cm) | Motor Firing Number and Table Reported | Type of Firing (lab or convergent) | Propellant Temperature (°F) | Firing Time (hr) | Pressure | Char Rate (mil/sec) | Char Rate / U. S. Rubber 3015 in Same Motor Firing |
|-------------|---|--------------------|--|------------------------------------|-----------------------------|------------------|----------|---------------------|--|
| VIII-B | Araldite DP-437 (10) Ciba Hardner (1) | 1.44 | M-275 (VII) | convergent | 5600 | 43.7 | high | 3.7 | --- |
| IV-B | Epon 815 (1) XR2000 (1) | 1.40 | M-275 (VII) | convergent | 5600 | 43.7 | high | 3.4 | --- |
| III | Epon 828 (10) NMA (9) Dibutyl maleate (8.36, 30%) | 1.56 | M-275 (VII) | convergent | 5600 | 43.7 | high | 4.3 | --- |
| II | Epon 828 (10) NMA (9) Aroclor 1248 (19, 50%) | 1.64 | M-275 (VII) | convergent | 5600 | 43.7 | high | 4.6 | --- |
| X-B | Araldite DP-437 (1) NMA (1) | 1.52 | M-300 (X) | convergent | 5600 | 66.1 | medium | 2.4 | 0.92 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | M-300 (X) | convergent | 5600 | 66.1 | medium | 2.6 | 1.00 |
| IV-A | Epon 815 (1) XR2000 (1) | 1.40 | PTM-3 (XII) | peripheral | 5600 | 63.5 | high | 3.3 | 1.10 |
| 3-A | Epon 828 (1) Thiokol EM206 (1) | 1.51 | PTM-3 (XII) | peripheral | 5600 | 63.5 | high | 3.2 | 1.07 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | PTM-3 (XII) | peripheral | 5600 | 63.5 | high | 3.0 | 1.00 |
| VIII-A | Araldite DP-437 (10) Ciba Hardner (1) | 1.44 | M-284 (XIII) | peripheral | 5600 | 62.3 | high | 3.2 | 1.19 |
| X-A | Araldite DP-437 (1) NMA (1) | 1.52 | M-284 (XIII) | peripheral | 5600 | 62.3 | high | 2.4 | 0.89 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | M-284 (XIII) | peripheral | 5600 | 62.3 | high | 2.7 | 1.00 |
| XIV-A | Epon 828 (1) Thiokol EM207 (1) | 1.50 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 4.1 | 1.28 |
| Ru 146 | U. S. Rubber 3015 | 1.24 | B-35 (XIV) | peripheral | 6500 | 46.3 | high | 3.2 | 1.00 |

- (a) The material having the best comparative char rate is the Araldite DP-437-NMA (1:1 ratio) (see X-B and X-13).
- (b) All other material had higher char rates than U. S. Rubber 3015. However, formulations IV and 3-A performed very well.
- (c) The dibutyl maleate (III)- and the Aroclor 1248 (II)-plasticized Guardian performed poorly. These two materials were also poor in their aging properties (see page 11) and, therefore, will not be considered as candidate materials for insulation application.

(4) New Fillers

The best insulator developed to date has been a 40-per cent-castor oil-modified Guardian filled with 20 per cent of potassium oxalate and 10 per cent of asbestos powder. However, the char rate for this material (1.1mil/sec, Table XI) is probably not realistic because of extensive swelling and voids that exist in the uncharred virgin material after a specimen is tested (see Figure 8). Char is calculated by subtracting the thickness of the remaining uncharred material from the initial thickness of the specimen; therefore, although a material may actually have a high char rate, one may calculate a negative char rate if the uncharred material swells extensively. Of course, this problem exists to a greater or lesser extent with most materials, and generally becomes quite pronounced when fillers that decompose at low temperatures are used. We have observed this same swelling problem with U. S. Rubber 3015 (with potassium oxalate filler). For this reason, and also because 3015 is no longer being considered as a candidate insulator, we plan to use V-44 and/or U. S. Rubber 3016 as comparative standards in the future.

B. MELAMINE RESINS

1. Flexibilization

Efforts to prepare a flexible melamine resin suitable for molding have continued. The various approaches and results are discussed below.

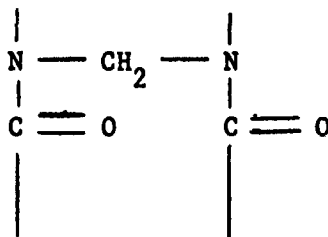
a. Co-Polymerization of Melamine or Methylol Melamine with Polyepoxides

Attempts were made to react the amino groups of melamine and the hydroxyl groups of methylol melamines with polyepoxides such as Syl-Kem 90 and Epon 812. Results from several trials of various formulations are summarized as follows:

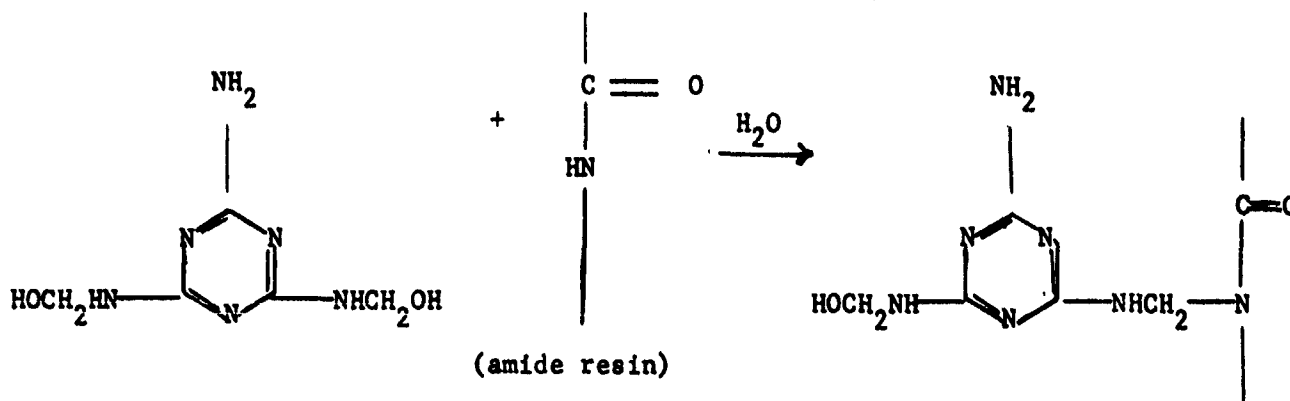
- (a) One part melamine would not dissolve in two parts Syl-Kem 90 at temperatures in excess of 300°C.
- (b) A homogeneous solution could not be obtained at elevated temperatures with 1 part dimethylol melamine and 2 parts Syl-Kem 90. The dimethylol melamine homopolymerized.
- (c) Flexible resins were prepared by co-reacting 1 part diallyl melamine with one part and with 2 parts of Syl-Kem 90. The solutions had to be cured above 125°C to prevent separation of the diallyl melamine. The cured resins were very flexible and soft.
- (d) Dimethylol diallyl melamine was prepared by heating 1 mol of diallyl melamine with 2 mols of 37 per cent aqueous formaldehyde under basic conditions. The solid product was washed with water and dried under vacuum. Approximately equal parts of this product and Epon 812 were mixed and cured at 150°C for 5 hours. The cured resin was hard and rigid.

b. Co-Polymerization of Dimethylol Melamine with a Polyamide

High-molecular-weight polyamides have been shown* to react with formaldehyde to form methylol derivatives which may further cross-link to resins of the following structure.



It was hoped that a similar condensation could be achieved between dimethylol melamine and Versamid 140, a commercial polyamide resin:

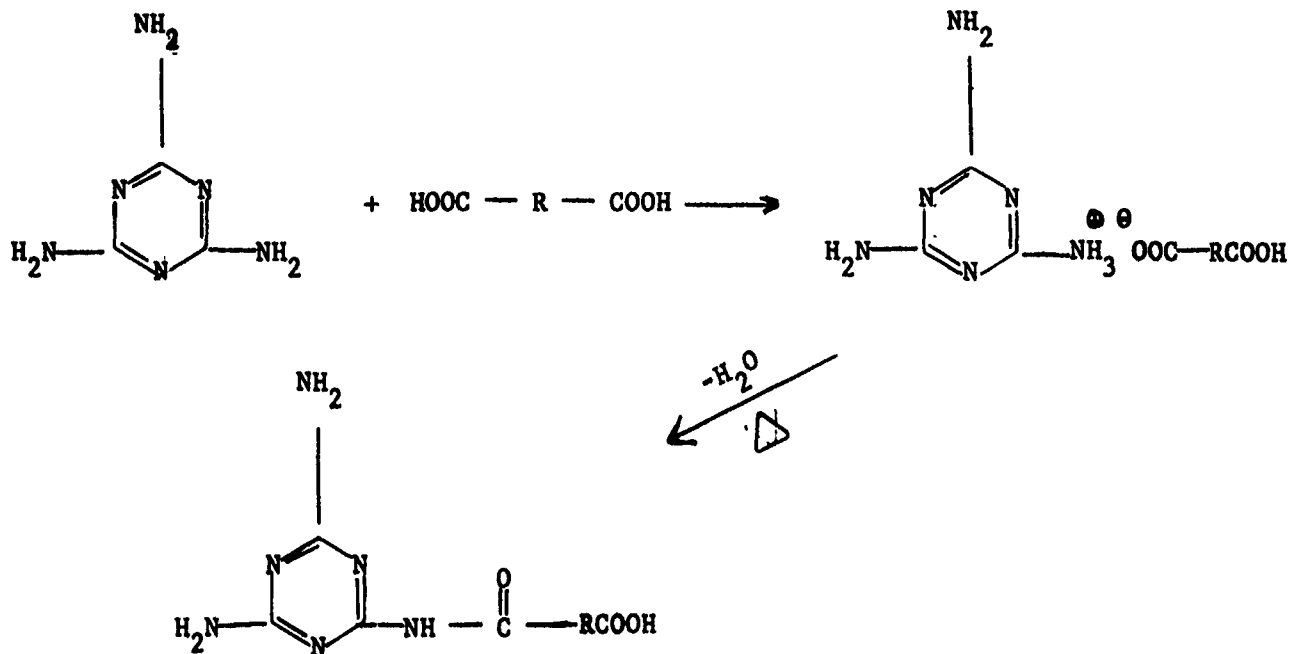


Continuation of the condensation step would lead to a polymeric material. However, dimethylol melamine homopolymerized in hot Versamid 140 without dissolving.

c. Co-Polymerization of Melamine with Polybasic Acids

Attempts to form salts between melamine and dibasic acids which could then be thermally decomposed to flexible polyamides were unsuccessful.

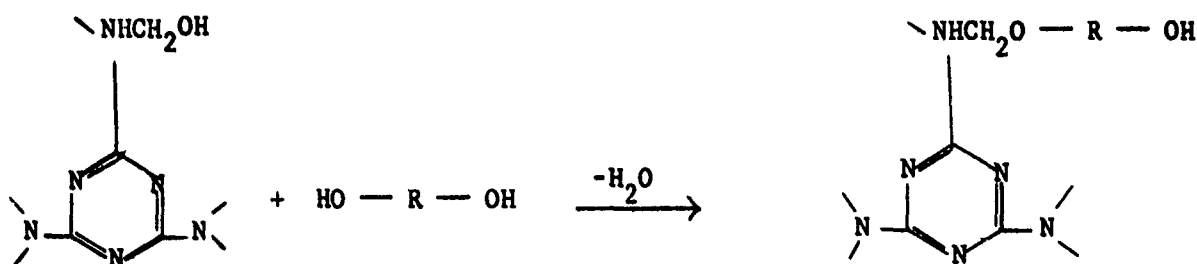
* T. L. Cairns, et al., J. Am. Chem. Soc., 71, 651 (1949).



Melamine and Empol 1014 dimer acid were incompatible at elevated temperatures. Melamine and sebacic acid yielded a hard, brittle, high melting (200 to 300°C) solid. The products were not identified, but may have been unreacted acid and melamine.

d. Co-Polymerization of Methylol Melamines with Polyols

Methylol melamines react with alcohols to form ethers. By using a diol or polyol, it may be possible to prepare polyethers containing the melamine unit, according to the following:

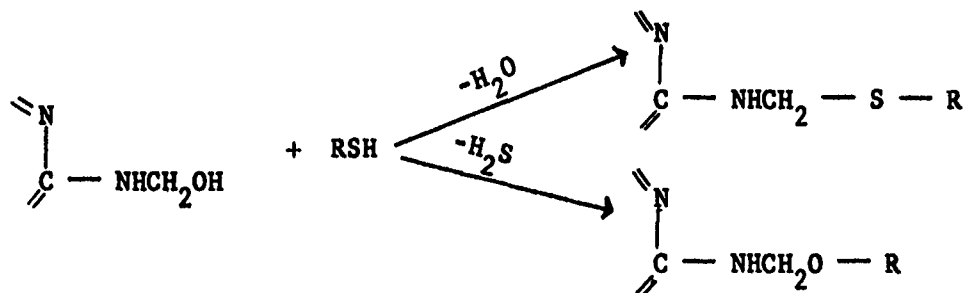


Hexamethylol melamine (HMM) was prepared by reacting an excess of 37 per cent aqueous formaldehyde with melamine under slightly basic conditions. The product was filtered off, washed with ethanol, dried at 50°C, and then used as follows:

- (1) Heating HMM under acid conditions with an excess of Plurocol TP-440 triol to the boiling point of the triol failed to give a solution or any evidence of reaction.
- (2) Heating HMM (4.45 grams) 1,4-butanediol (3.22 grams), and butyl alcohol (3.92 grams) under acid conditions at 120°C for 30 minutes gave a viscous, jelly-like solution. A hard, brittle material resulted when a small portion of this product was heated at 150°C for 3 hours.
- (3) A hot saturated solution of HMM in butanediol was prepared by slowly adding HMM to the hot diol until no more dissolved. The solution was poured into an aluminum dish and cooled. An equivalent amount of Epon 828 and a few drops of BDMA were added. This homogeneous solution was cured at 125°C for 5 hours and then at 150°C for about 16 hours. A hard, rigid material was obtained.

e. Co-Polymerization of Methylol Melamine with Polythiols

Since alcohols react with methylol melamines to form ethers, it may be possible for a similar type of condensation to occur between a thiol and a methylol melamine with the elimination of H_2O to form the sulfide and/or the elimination of H_2S to form the ether.



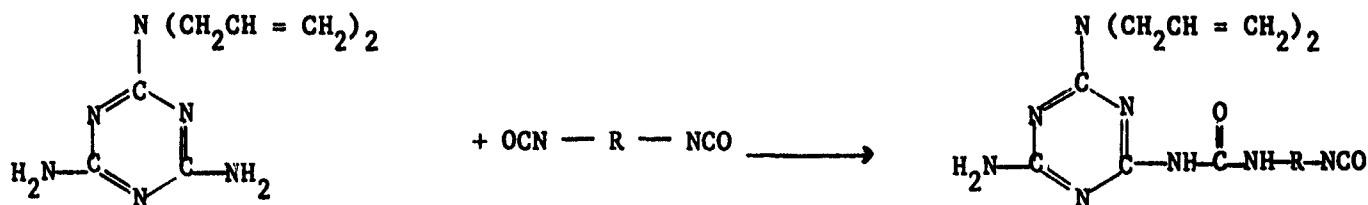
Thiokol's LP-8, a liquid polysulfide containing SH groups, was reacted with hexamethylol melamine and dimethylol diallyl melamine, with the following results:

- (1) Heating 2 grams of HMM with 5 grams of LP-8 to 125°C under acid conditions resulted in only the slow evaporation of the LP-8.
- (2) Approximately equal parts of dimethylol diallyl melamine and LP-8 were mixed and then cured at 150°C for 6 hours. While still warm, the material was soft and flexible, but on cooling it hardened and remained only slightly flexible.

f. Co-Polymerization of Melamines with Isocyanates

Amines react with isocyanates to give substituted ureas.

A similar reaction was attempted with diallyl melamine and a diisocyanate.

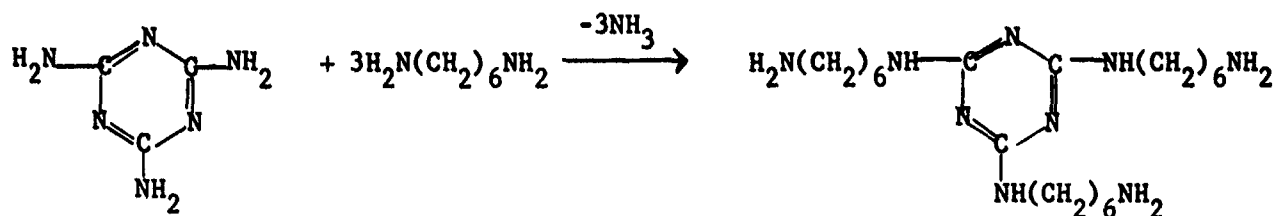


Diallyl melamine and toluene diisocyanate were reacted in the mol ratios of 1:1 and 1:2. In the first case there is only sufficient toluene diisocyanate to react with only two of the hydrogens attached to nitrogen in the DAM, while in the second case, there is sufficient isocyanate to react with all four hydrogen atoms. Cure temperature was 125°C. Both formulations yielded white, hard, brittle products. Substituting benzoguanamine for the diallyl melamine did not result in a flexible material.

g. Attempted Preparation of N², N⁴, N⁶-Trihexylamine Melamine

Trihexylamine melamine would be an ideal intermediate for the preparation of flexible melamine resins since (1) it should be reactive with many of the flexibilizers (which has been found not to be the case with melamine and methylol melamines), and (2) it can be polymerized through addition reactions instead of condensation reactions. This latter type is undesirable because it usually is accompanied by undesirable volume changes in the resin.

Melamine has been reported to react with amines to yield N-substituted melamines by the elimination of one, two, or three mols of ammonia. By reacting hexamethylene diamine with melamine, one would expect to obtain N², N⁴, N⁶tri-n-hexylamine.



This reaction was attempted in the following manner: To 1.43 mols of hexamethylene diamine dissolved in 300 ml of dry ethylene glycol at 190°C was added 0.2 mol (25 gm) of melamine. The addition was completed in 2 hours and the homogeneous solution was heated for an additional 2.25 hours. After removal of the solvent under vacuum, the reaction flask was

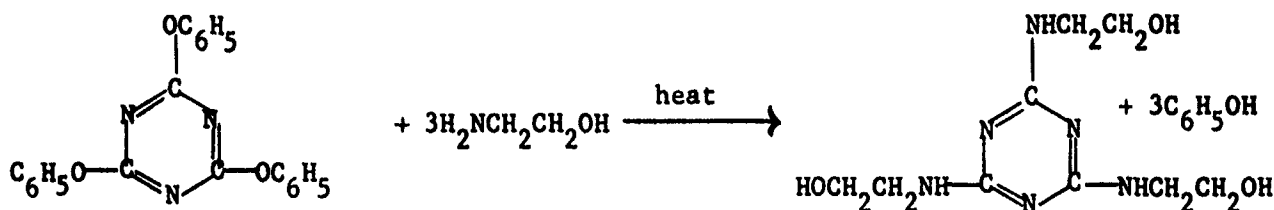
cooled and the contents filtered through a Buchner funnel. Eighteen grams (72 per cent) of melamine was recovered. Refiltration of the filtrate (after standing overnight) gave 0.7 gm of a solid for which the infrared spectrum differed from melamine. The lack of -NH_2 absorption, however, indicates that it is not the desired product. The remaining 25 per cent of the initial melamine is present in one form or another in the residue filtrate composed of mostly the hexamethylene diamine and some ethylene glycol. Attempts to account for the remaining 25 per cent of the melamine were unsuccessful.

h. Preparation of Triphenyl Cyanurate and Attempted Preparation of $\text{N}^2, \text{N}^4, \text{N}^6$ -tris-(β -hydroxyethyl)-Melamine

Many substituted melamines are readily prepared from cyanuric chloride and the amine. However, in certain cases, this synthesis is not practical because of the difficulty in the isolation of the product. This is reported to be the case with $\text{N}^2, \text{N}^4, \text{N}^6$ -tris-(β -hydroxyethyl)-melamine, an intermediate of potential use for the synthesis of flexible melamine resins. A procedure for the synthesis of this intermediate from triphenyl cyanurate and monoethanolamine has been reported,* and we have investigated this approach.

Triphenyl cyanurate was prepared in 89 per cent yield from cyanuric chloride and phenol according to the procedure developed by Schaefer, Thurston, and Dudley.**

This material was used in the attempted preparation of $\text{N}^2, \text{N}^4, \text{N}^6$ -tris-(β -hydroxyethyl)-melamine by the following reaction:



* Thurston, et al., J. Am. Chem. Soc., 73, 2992 (1951).

** Schaefer, Thurston, and Dudley, J. Am. Chem. Soc., 73, 2990 (1951).

In a flask, 0.139 mole of triphenyl cyanurate and 0.556 mole of monoethanolamine were heated at 177°C for 6.5 hours. The literature reference called for 5 hours at 210°C; however, in our case, the mixture refluxed at 177°C and 210°C could not be obtained. At the end of the reaction, a vacuum was applied, and most of the volatile material was distilled. The reaction mixture was taken up in hot butanol. Much more butanol was needed than specified.* The hot solution was treated with activated carbon, filtered, and allowed to cool. The solid was filtered and recrystallized from butanol after treatment with activated carbon. The melting point of this product was above 180°C; the literature value for tris-(β -hydroxyethyl)-melamine is 98-100°C.

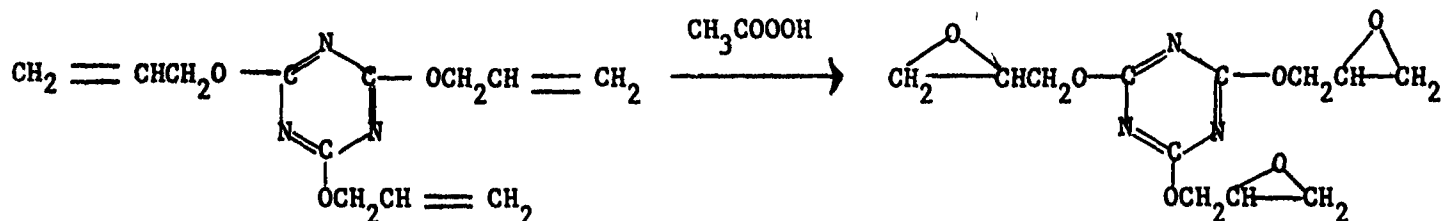
The chemical structure of this material is not too clear. It is water soluble, and its aqueous solution is strongly basic. The infrared spectrum has been made, but no useful information could be interpreted from it. Several crops of crystals have been obtained from the butanol solvent by repetitive partial evaporation of the solvent, allowing the material to crystallize overnight and then filtering off the crystals.

Prior to further effort on the identification of the various crops of crystals, the triphenyl cyanurate-ethanolamine reaction will be repeated. Only if the reaction is again unsuccessful will some attempt be made to identify the products from this reaction.

i. Preparation and Polymerization of Triglycidyl Cyanurate

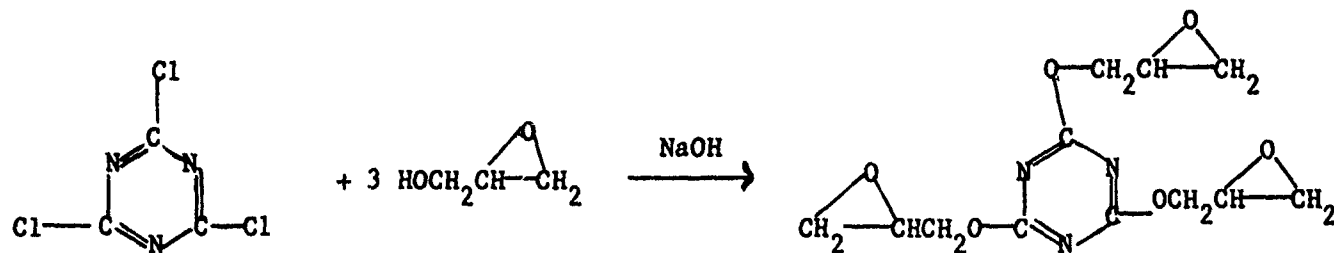
Triglycidyl cyanurate is a water-white, very viscous liquid, soluble in benzene, acetone, and chloroform. It has been prepared by reacting cyanuric chloride with an excess of glycidol under basic conditions. An alternative and perhaps much cheaper preparation would be the direct epoxidation of triallyl cyanurate:

* Schaefer, Thurston, and Dudley, J. Am. Chem. Soc., 73, 2990 (1951).



This latter reaction was attempted using the following procedure. To an excess of peracetic acid (40 per cent peracid in acetic acid) in chloroform was added a small amount of sodium acetate to remove traces of sulfuric acid present in the commercial peracetic acid. A solution of triallyl cyanurate in chloroform was then added dropwise into the stirred mixture. The reaction mixture was stirred for an additional hour at room temperature and then for 7 hours at 60°C, after which it was allowed to stand for 90 hours at room temperature. The chloroform, acetic acid, and remaining peracetic acid were then distilled off under vacuum, water added to the residue, and the mixture extracted with chloroform. A solid material which was insoluble in the water and chloroform was collected by filtration. From the chloroform layer, 2.1 gm of a viscous liquid was isolated. The infrared spectra showed this material to be essentially triallyl cyanurate contaminated with a small amount of acetic acid. If any triglycidyl cyanurate were present, it would have appeared in the chloroform extract. The insoluble solid has not been identified; however, its infrared spectrum indicates it to be some derivative of the triallyl cyanurate.

Triglycidyl cyanurate was successfully prepared in 89 per cent yield by reacting cyanuric chloride with glycidol under basic conditions:



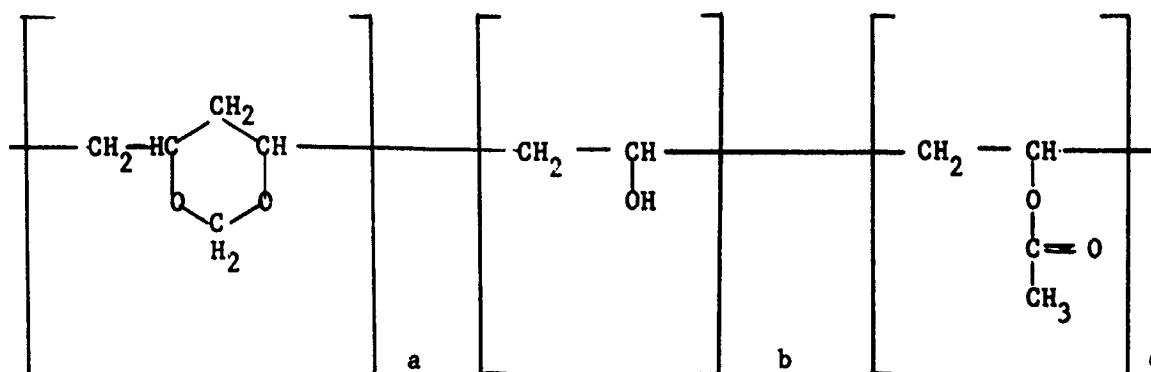
The procedure used was essentially the one developed by Schaefer, Thurston, and Dudley.*

The triglycidyl cyanurate was co-reacted with several modifiers. Results are reported in Table XVIII. With EM207 (and it may also be the case for other modifiers), the exotherm of the polymerization is very high. Unless it is controlled, extensive charring will occur. By allowing the formulation to stand at room temperature before curing at 125°C, charring can be avoided; this is attributed to either the partial loss of the catalyst (BDMA) through evaporation and/or partial curing at room temperature, which would reduce the exotherm of the reaction when cured later at elevated temperature.

An attempt to co-react the triglycidyl cyanurate with QZ-8-0914, a difunctional silicone epoxy resin, appeared to result in a heterogeneous polymerization of the two components. As indicated above, this triepoxide is very reactive and some care must be used in its preparation and use.

1. Reaction of Dimethylol Melamine with Polyvinyl Acetal Resins

Formvar,** a polyvinyl formal resin, may be represented by the following structure:



These resins are reported to react with methylol melamines. However, attempts to prepare flexible resins with 5 to 30 per cent of Formvar 12/85 were unsuccessful. All castings were rigid and brittle.

* Schaefer, Thurston, and Dudley, J. Am. Chem. Soc., 73, 2990 (1951).

** Shawnigan Resins

Table XVIII
Modifications of Triglycidyl Cyanurate

| Formulation Number | Formulation ^a | Cure Conditions | | Results |
|-----------------------|------------------------------------|--------------------------|----------------|---|
| | | Temperature (°C) | Time (hr) | |
| 148-I | Triglycidyl cyanurate EM207 | 125 | 0.25 | Cured to a rigid material with much charring and smoke. |
| 149-I | Triglycidyl cyanurate EM207 | Rm. Temp. then 125 | 1.5 1 | Viscous liquid. Flexible. |
| 150-I | Triglycidyl cyanurate QZ-8-0914 | 100 | 22 | A rigid orange-yellow waxy solid which appeared to cure in two separate phases. |
| 151-I | Triglycidyl cyanurate EM207 | 75 then 150 | 1.75 7 min. | Viscous liquid. Cured to a rigid material with much charring and smoke. |

a. All components 1:1 by weight with 2 per cent BDMA catalyst.

2. Preparation of Filled Melamine Resins

Attempts were made to prepare an asbestos-filled molding from the flexible diallyl melamine-QZ-8-0914 resin system. Equal parts of diallyl melamine and QZ-8-0914 were dissolved in warm acetone. The asbestos was added to this solution, and the acetone evaporated under vacuum at 50°C to give a material consisting of 60 per cent resin and 40 per cent asbestos fiber. Attempts to cure this material under conditions sufficient to cure the pure resin failed. Diallyl melamine is not very soluble in the QZ-8-0914 and will precipitate if the solution is not kept above 120°C. In the above case, when the acetone was evaporated, diallyl melamine undoubtedly precipitated on the asbestos, and then apparently, upon heating up during molding, it did not properly redissolve.

C. FLEXIBLE PHENOLIC RESINS

1. Determination of Physical Properties

Previously, A-stage phenol-formaldehyde resins which were modified for use as flexible insulators were prepared exclusively in the laboratory. However, because of practical and economic considerations involved in the production of prototype insulators, preliminary investigations were started during this period to evaluate a commercially available A-stage phenol-formaldehyde resin.

The first commercial resin evaluated was a Bakelite stage "A" phenol-formaldehyde resin, B2620. The mechanical properties of several B2620-Syl-Kem 90 formulations were determined. The results, shown in Table XIX, are compared with the mechanical properties of the standard phenolic resin also modified with Syl-Kem 90 and previously evaluated.

The tensile strengths of B2620-Syl-Kem 90 mixtures were relatively low and did not increase appreciably with resin concentration. However, the high tensile strengths of the standard phenolic-Syl-Kem 90 formulations changed rapidly with resin content. These results indicate that the B2620 has fewer available cross-link sites and that it probably has a higher molecular weight than the standard phenolic resin.

Table XIX
Physical Properties of Modified Bakelite B2620 and Standard Phenolic Resins

| Formulation | Cure Time (hr) | Mechanical Properties ^a | | |
|------------------------------|---------------------------------------|------------------------------------|--------------------------|-------------------------|
| | | Tensile Strength (psi) | Elongation (per cent) | Secant Modulus (psi) |
| B2620:Syl-Kem 90 | | | | |
| 30:70 | 0.75 ^b 2.5 ^c | Poor - not tested | | |
| 35:65 | 0.75 2.25 | 134 | 62 | 220 |
| 40:60 | 0.50 2.25 | 287 | 93 | 293 |
| 50:50 | 0.50 2.25 | 226 | 71 | 316 |
| Standard Phenolic:Syl-Kem 90 | | | | |
| 30:70 ^d | 3.0 ^c | 1040 | 270 | 400 |
| 40:60 ^d | 3.0 | 2055 | 74 | 300 |
| 50:50 ^d | 3.0 | 3290 | 17 | 39,200 |

a. Gage length: 2 inches; testing speed: 20 in/min.

b. Gel time at 150°C.

c. 150°C and 1,000 psi; flash molded.

d. Previously reported, First Annual Summary Report, DA-036-ORD-332SRD, July, 1961, p. 44.

The elongations of cured B2620-Syl-Kem 90 are higher than those of the corresponding standard phenolic Syl-Kem 90 materials in the range of 40 to 50 per cent resin. This advantage definitely favors the use of B2620 resin since elongation becomes a critical insulator property at high resin content.

2. Oxyacetylene-Torch Test Results

Torch test results for a variety of flexible phenolic materials filled with 45 per cent of asbestos were obtained during this report period as shown in Table XX. The indices, I_{400} and I_{600} , were used as the base for rating the effectiveness of these materials as insulators. The results indicate exceptionally good insulation characteristics for the majority of the flexible phenolic materials tested.

The materials can be grouped according to composition:

(1) nonyl phenolic-Syl-Kem 90-asbestos, (2) standard phenolic-Syl-Kem 90-asbestos, (3) Bakelite B2620-Syl-Kem 90-asbestos, and (4) standard phenolic-nonyl phenolic mixtures-Syl-Kem 90-asbestos. The best insulator tested in these four groups was the 40:60 nonyl phenolic-Syl-Kem 90 composition ($I_{400} = 180.1$). In the case of the 50:50 and 60:40 nonyl phenolic-Syl-Kem 90 materials, the insulation indices were 137 and 133, respectively, while the 65:35 composition had an insulation index of only 114. This sharp decrease in I_{400} could possibly have resulted because the specimens became more thermoplastic as the nonyl phenolic resin content increased. If, in the testing of these materials with high resin content, the nonyl phenolic softens and flows away from the cavity formed by the impinging gas flame, then lower insulation indices will result. The shapes of the nonyl phenolic-Syl-Kem 90 specimens after burning supported this argument of plastic flow. These materials were tested in the convergent section of a rocket motor where more significant results were obtained (Table XXIV).

Table XX
Oxyacetylene Torch-Test^a Results for Asbestos-Filled Phenolics

| Formulation ^b (per cent) | Life, minutes ^c Pressure (psi) | Time (hr) | Char Rate (mil/sec) | Average Char Rate (mil/sec) | Erosion Rate (mil/sec) | Average Erosion Rate (mil/sec) | Weight Loss (per cent/sec) | T _{400°F} (sec/in) | Average T _{400°F} (sec/in) | T _{400°F} Rank | T _{600°F} (sec/in) | Average T _{600°F} (sec/in) | T _{600°F} Rank | Δt _{400-600°F} (sec/in) |
|--|---|--------------|------------------------|-----------------------------------|------------------------------|--------------------------------------|-------------------------------|--------------------------------|---|----------------------------|--------------------------------|---|----------------------------|-------------------------------------|
| Standard ^d phenolic 40-60-40 | 3000 | 2.75 | 6.5 | 6.80 | 4.6 | 4.86 | 0.96 | 137.8 | 134.4 | 10 | 146.0 | 141.3 | 10 | 9.2 |
| | | 2.25 | 7.1 | | 5.0 | | 0.98 | 131.0 | | | 137.5 | | | 6.5 |
| " | 2000 | 2.25 | 4.7 | 4.95 | 3.7 | 3.40 | 0.82 | 170.3 | 177.2 | 3 | 179.8 | 187.0 | 1 | 8.5 |
| | | 2.75 | 5.0 | | 3.1 | | 0.75 | 134.0 | | | 195.2 | | | 11.2 |
| " | 1000 | 2.25 | 5.0 | 4.90 | 3.8 | 3.95 | 0.82 | 168.1 | 168.1 | 4 | 173.3 | 176.9 | 4 | 5.2 |
| | | 2.75 | 5.8 | | 3.0 | | 0.82 | 168.0 | | | 180.5 | | | 12.5 |
| 0-10 | 3000 | 2.25 | 5.0 | 5.15 | 3.2 | 3.15 | 0.76 | 177.6 | 177.5 | 2 | 186.8 | 184.9 | 3 | 9.2 |
| | | 2.75 | 5.3 | | 3.3 | | 0.76 | 177.3 | | | 193.0 | | | 5.7 |
| Asbestos 82-20 40-60-40 | 3000 | 2.25 | 6.4 | 6.50 | 5.0 | 5.05 | 1.06 | 127.2 | 132.1 | 12 | 132.1 ^h | 139.5 | 11 | 4.9 |
| | | 2.75 | 7.0 | | 5.1 | | 1.15 | 136.9 | | | 146.8 ^h | | | 7.3 |
| " | 2000 | 2.25 | 7.7 | 7.35 | 5.4 | 5.70 | 1.27 | 112.8 | 119.8 | 13 | 117.9 ^h | 126.3 | 13 | 5.1 |
| | | 2.75 | 8.3 | | 6.0 | | 0.99 | 126.8 | | | 137.5 ^h | | | 10.7 |
| " | 1000 | 2.25 | 6.5 | 6.25 | 5.3 | 5.40 | 1.06 | 137.2 | 138.4 | 8 | 142.8 ^h | 146.9 | 8 | 5.3 |
| | | 2.75 | 7.0 | | 5.5 | | 0.96 | 139.5 | | | 150.9 ^h | | | 11.4 |
| Asbestos 60-40 40-60-40 | 3000 | 2.25 | 7.5 | 7.50 | 5.3 | 5.30 | 0.84 | 180.1 | 180.1 | 1 | 186.5 | 186.5 | 2 | 6.4 |
| | | 2.75 | 8.3 | | 6.4 | | 0.78 | 129.1 | 138.2 | 9 | 132.6 ^h | 142.7 | 9 | 5.5 |
| " | 2000 | 2.25 | 7.5 | 7.55 | 4.9 | 5.65 | 0.69 | 147.2 | 147.2 | | 152.8 ^h | | | 5.6 |
| " | 1000 | 2.25 | 5.4 | 5.95 | 5.1 | 5.35 | 0.81 | 131.2 | 132.9 | 14 | 133.5 ^h | 135.4 | 12 | 2.3 |
| | | 2.75 | 6.5 | | 5.6 | | 0.79 | 134.5 | | | 137.5 ^h | | | 2.7 |
| Asbestos 40-60 40-60-40 | 3000 | 2.25 | 5.5 | 5.55 | 5.4 | 5.00 | 0.45 | 113.2 | 113.9 | 14 | 117.8 ^h | 120.5 | 14 | 4.9 |
| | | 2.75 | 5.5 | | 4.9 | | 0.36 | 114.5 | | | 123.1 ^h | | | 8.6 |
| Asbestos 20-80 40-60-40 | 3000 | 2.25 | 4.7 | 4.70 | 4.0 | 4.00 | 0.59 | 164.4 | 164.4 | 5 | 171.0 | 171.0 | 5 | 6.6 |
| " | | 2.75 | 5.3 | | 4.8 | | 0.67 | 144.0 | 144.0 | 7 | 150.5 ^h | 150.5 | 7 | 6.5 |
| Asbestos 10-90 40-60-40 | 3000 | 2.25 | 5.4 | 5.10 | 4.5 | 4.50 | 0.82 | 163.2 | 163.2 | 6 | 166.9 | 166.9 | 6 | 3.7 |

NOTES:

- Naval Ordnance Laboratory Standard Conditions.
- All resins filled with 45 per cent of asbestos.
- Test time, no pressure.
- The values for T_{400°F} were determined by extrapolation of the time-temperature trace from 400°F.
- Post-cured for 3.5 hours at 150°C.
- T₀ = initial specimen thickness (mils or inches).
- T_f = final uncharred thickness (mils or inches).
- T_f = final thickness (mils).
- W₀ = initial weight (grams).
- W_f = final weight (grams).
- TBT = total burning time (seconds).
- T_{400°F} = time for back of specimen to reach 400°F (seconds).
- T_{600°F} = time for back of specimen to reach 600°F (seconds).
- Char Rate = (T₀ - T_f)/TBT (mil/sec).
- Erosion Rate = (W₀ - W_f)/TBT (mil/sec).
- Weight Loss = (W₀ - W_f)/100/W₀ (T weight loss/sec).
- Insulation Index at temperature T = T_f = t_f/T₀ (sec/in).

The second group of insulators investigated consisted of standard phenolic-Syl-Kem 90 mixtures. The 50:50, 40:60, 30:70, and 20:80 compositions had I_{400} values of 177.5, 168.1, 177.2, and 134.4, respectively. These materials were rated second, fourth, third, and tenth best insulators in that order. This group of promising materials has been tested in motor firings and the results are reported in Table XXI.

The third group contained Bakelite B2620 stage "A" phenol-formaldehyde resin. Because the insulation indices of the B2620 Syl-Kem 90 formulations are 45 to 48 units lower than the corresponding standard phenolic formulations, the B2620 materials will not be motor-tested. This resin may find use as a modifier in the standard phenolic system.

The fourth group were mixtures of the standard phenolic and nonyl phenolic resins. The 10:30:60, 20:20:60, and 30:10:60 standard phenolic-nonyl phenolic-Syl-Kem 90 compositions had I_{400} values of 164.4, 144.0, and 163.2. These materials were rated the fifth, seventh, and sixth best insulators. These materials have also been motor tested and the data is reported in Table XXII.

3. Static-Motor Testing

The techniques involved in preparing specimens for convergent-section motor firings have been described previously. In Tables XXI through XXIV are reported the results for some flexible phenolic resins. Photographs of the tested specimens are shown in Figures 14, 15, and 7.

The most promising flexible phenolic system has been the standard phenolic-Syl-Kem 90 formulation (1:1 ratio). In Table XXV the motor firing results for this material containing various fillers are summarized and compared to U. S. Rubber 3015. The asbestos fiber-potassium oxalate composite filler is more effective than either asbestos or potassium oxalate fillers alone. Formulation 7-19E performed as good as or better than U. S. Rubber 3015 control. Because the 3015 specimen exhibited unusual central swelling in Firing PYB-5 (see Figure 14), it was therefore necessary to report two char rates: 3.5 mil/sec at the center and 5.4 mil/sec at the edge. Previous experience with U. S. Rubber 3015 in similar firings indicate that 3.5 mil/sec is probably more accurate.

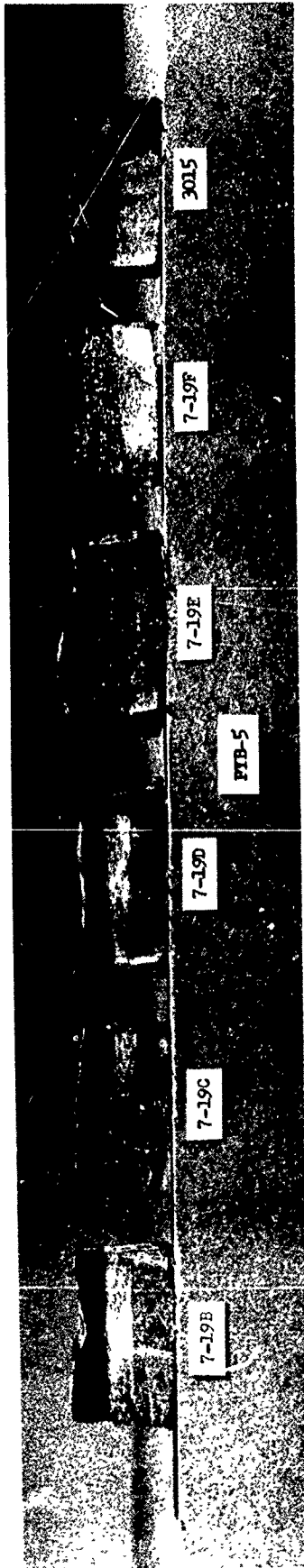


Figure 14.

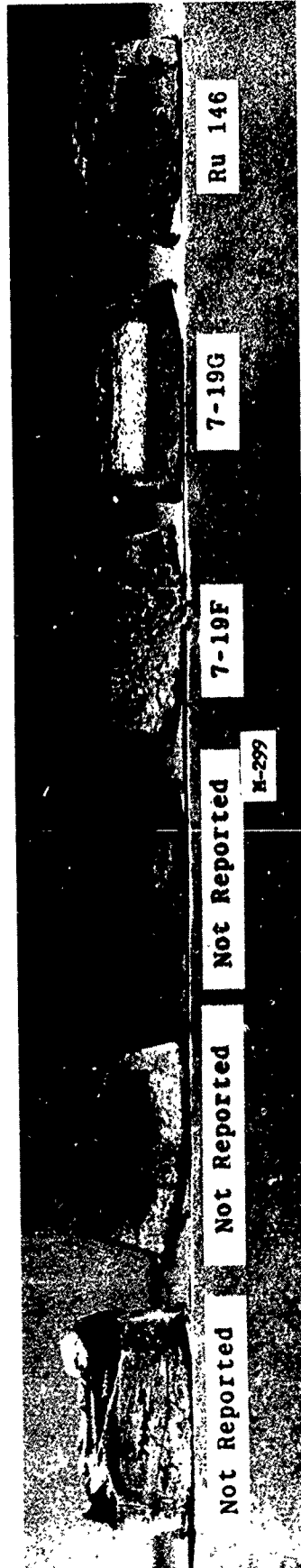


Figure 15.

Figures 14, 15. Convergent-Section Test Specimens from Firings PYB-5 and M-299.

Table XXI
Convergent-Section Motor Firing M-282 Results for Filled Phenolic Resins^a

| Formulation Number | Formulation (per cent) | Resin Composition (per cent) | Curing Conditions | | Time (hr) | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate x Density |
|--------------------|---|--|-------------------|----------------|-----------|--------------------|---------------------|---------------------|
| | | | Temperature (°C) | Pressure (psi) | | | | |
| 7-12-B | 55 resin ^b 45 asbestos | 50 standard phenolic ^e 50 Syl-Kem 90 | 150 | 3000 | 0.25 | 1.52 | 2.6 | 4.0 |
| | | | 150 | | 2.75 | | | |
| 7-12-C | 55 resin 45 asbestos | 40 standard phenolic 60 Syl-Kem 90 | 150 | 3000 | 0.25 | 1.49 | 3.3 | 4.9 |
| | | | 150 | | 2.75 | | | |
| 7-12-D | 55 resin 45 asbestos | 30 standard phenolic 70 Syl-Kem 90 | 150 | 3000 | 0.25 | 1.45 | 3.6 | 5.2 |
| | | | 150 | | 2.75 | | | |
| 7-12-E | 55 resin 45 asbestos | 20 standard phenolic 80 Syl-Kem 90 | 150 | 3000 | 0.75 | 1.39 | 4.6 | 6.4 |
| | | | 150 | | 2.25 | | | |
| PA 12 | Phenolic resin ^c asbestos felt (41 RPD) | --- | -- | -- | -- | 1.50 | 3.3 | 5.0 |
| Ru 121 | U. S. Rubber 3015 ^d | | -- | -- | -- | 1.24 | 2.3 | 2.8 |

- a. Length of firing: 30.2 sec; flame temperature: 5600°F; high pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
b. 3R100 asbestos fiber
c. Included in firing as a comparative standard. One of the best commercially available rigid insulators.
d. Included in firing as a comparative standard.
e. Atlantic Research Corporation phenol-formaldehyde resin.

Table XXII
Convergent-Section Motor Firing PVB-5 Results for Filled Phenolic Resins^a

| Formulation Number | Formulation (per cent) | Resin Composition (per cent) | Curing Conditions | | Density (gm/cu cm) | Char Rate (mil. sec) | Char Rate x Density |
|--------------------|--|--|-------------------|----------------|--------------------|----------------------|---------------------|
| | | | Temperature (°C) | Pressure (psi) | | | |
| 7-19-B | 55 resin ^b 45 asbestos | 10 standard phenolic ^d 30 nonyl phenolic ^e 60 Syl-Kem 90 | 150 | 3000 | 1.41 | 1.5 | 8.3 |
| | | | 150 | | | 1.5 | |
| 7-19-C | 55 resin 45 asbestos | 20 standard phenolic 20 nonyl phenolic 60 Syl-Kem 90 | 150 | 3000 | 1.46 | 1 | 9.5 |
| | | | 150 | | | 2 | |
| 7-19-D | 55 resin 45 asbestos | 30 standard phenolic 10 nonyl phenolic 60 Syl-Kem 90 | 150 | 3000 | 1.42 | 3 | 7.7 |
| | | | | | | | |
| 7-19-E | 55 resin 22.5 asbestos 22.5 potassium oxalate ^c | 50 standard phenolic 50 Syl-Kem 90 | 150 | 3000 | 1.50 | 3 | 5.0 |
| | | | | | | | |
| 7-19-F | 55 resin 45 potassium oxalate | 50 standard phenolic 50 Syl-Kem 90 | 150 | --- | 1.50 | 3 | 7.5 |
| | | | | | | | |
| R-146 | U. S. Rubber Insulator 3015 ^f | | -- | -- | 1.24 | -- | 6.7 4.3 |

^a Length of firing: 46.0 sec; flame temperature: 6500°F. high pressure; motor quenched with nitrogen at end of firing to prevent after burning of specimen.
^b 3R100 asbestos
^c Fisher certified potassium oxalate (K₂C₂O₄·H₂O)
^d Standard phenolic - Atlantic Research Corporation phenol-formaldehyde resin.
^e Nonyl phenolic - Atlantic Research Corporation nonyl phenol-formaldehyde resin.
^f Comparative standard.

Table XXIII
Convergent-Section Motor Firing M-299 Results for Filled Phenolic Resins^a

| Formulation Number | Formulation (per cent) | Resin Composition (per cent) | Curing Conditions | | | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate x Density |
|--------------------|---|--|-------------------|----------------|-----------|--------------------|---------------------|---------------------|
| | | | Temperature (°C) | Pressure (psi) | Time (hr) | | | |
| 7-19-E | 55 resin | 50 standard phenolic ^d 50 Syl-Kem 90 | 150 | 3000 | 3 | 1.50 | 2.1 | 3.1 |
| | 22.5 asbestos ^b 22.5 potassium oxalate ^c | | | | | | | |
| 7-19-G | 39.0 resin | 40 standard phenolic 60 Syl-Kem 90 | 150 | -- | 3 | -- | 3.1 | -- |
| | 62.0 potassium oxalate ^c | | | | | | | |
| Ru 146 | U. S. Rubber Insulator 3015 ^e | | -- | -- | -- | 1.74 | 3.1 | 3.8 |

- a. Length of firing: 68.1 sec; flame temperature: 5600°F; high pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimens.
b. 3R100 asbestos
c. Fisher certified potassium oxalate ($K_2C_2O_4 \cdot H_2O$)
d. Standard phenolic - Atlantic Research Corporation phenol-formaldehyde resin.
e. Comparative standard.

Table XXIV

Convergent-Section Motor Firing M-300 Results for Filled Phenolic Resins^a

| Formulation Number | Formulation (per cent) | Resin Composition (per cent) | Curing Conditions | | | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate × Density |
|--------------------|--------------------------------------|---|-------------------|----------------|--------------------|--------------------|---------------------|---------------------|
| | | | Temperature (°C) | Pressure (psi) | Time (hr) | | | |
| 7-19-A | 55 resin 45 asbestos | 40 nonyl phenolic 60 Syl-Kem 90 | 150 | 3000 | 6 ^e | 1.43 | 3.5 | 5.0 |
| | | | 150 | | 9 ^f | | | |
| | | | 150 | | 18.75 ^g | | | |
| 7-16-A | 55 resin 45 asbestos ^b | 50 nonyl phenolic ^c 50 Syl-Kem 90 | 150 | 3000 | 4 ^e | 1.39 | 3.0 | 4.2 |
| | | | 150 | | 7.5 ^f | | | |
| | | | 150 | | 3.5 ^g | | | |
| 7-16-B | 55 resin 45 asbestos | 60 nonyl phenolic 40 Syl-Kem 90 | 150 | 3000 | 3.75 ^e | 1.37 | 2.7 | 3.7 |
| | | | 150 | | 8 ^f | | | |
| | | | 150 | | 3.5 ^g | | | |
| 7-16-C | 55 resin 45 asbestos | 65 nonyl phenolic 35 Syl-Kem 90 | 150 | 3000 | 3.75 ^e | 1.42 | 2.9 | 4.1 |
| | | | 150 | | 8 ^f | | | |
| | | | 150 | | 3.5 ^g | | | |
| Ru 146 | U. S. Rubber Co. 3015 ^d | | --- | -- | -- | 1.24 | 2.6 | 3.2 |

a. Length of firing: 66.1 sec; flame temperature: 5600°F; medium pressure; motor quenched with nitrogen at end of firing to prevent after-burning of specimen.

b. 3R100 asbestos fiber.

c. Atlantic Research Corporation nonyl phenol-formaldehyde resin.

d. Comparative standard.

e. Pre-cure.

f. Pressure cure.

g. Post-cure.

Table XXV

Comparison of Char Rates of a Flexible Phenolic Resin Containing Various Fillers

| Code Number | Formulation (per cent) | Density (gm/cu cm) | Motor Firing ^a Number and Table Reported | Propellant Temperature (°F) | Firing Time (sec) | Char Rate (mil/sec) | Char Rate/ Char Rate U. S. Rubber 3015 in same Motor Firing |
|----------------|---------------------------|-----------------------|---|-----------------------------------|-------------------------|---------------------------|---|
| | | | | | | | |
| 7-12-B | 27.5 standard phenolic | 1.52 | M-282 (XXI) | 5600 | 30.2 | 2.6 | 1.13 |
| | 27.5 Syl-Kem 90 | | | | | | |
| | 45.0 asbestos fiber | | | | | | |
| Ru 121 | U. S. Rubber 3015 | 1.24 | M-282 (XXI) | 5600 | 30.2 | 2.3 | 1.00 |
| 7-19-E | 27.5 standard phenolic | 1.50 | PYB-5 (XXII) | 6500 | 46.0 | 3.3 | 0.94 |
| | 27.5 Syl-Kem 90 | | | | | | |
| | 22.5 asbestos fiber | | | | | | |
| | 22.5 potassium oxalate | | | | | | |
| 7-12-F | 27.5 standard phenolic | 1.50 | PYB-5 (XXII) | 6500 | 46.0 | 5.2 | 1.48 |
| | 27.5 Syl-Kem 90 | | | | | | |
| | 45.0 potassium oxalate | | | | | | |
| Ru 146 | U. S. Rubber 3015 | 1.24 | PYB-5 (XXII) | 6500 | 46.0 | 3.5 | 1.00 |
| 7-19-E | 27.5 standard phenolic | 1.50 | M-299 (XXIII) | 5600 | 68.1 | 2.1 | 0.68 |
| | 27.9 Syl-Kem 90 | | | | | | |
| | 22.5 asbestos fiber | | | | | | |
| | 22.5 potassium oxalate | | | | | | |
| Ru 146 | U. S. Rubber 3015 | 1.24 | M-299 (XXIII) | 5600 | 68.1 | 3.1 | 1.00 |

a. All firings convergent-section tests at high pressure.

The better performance of 7-19E compared to 7-12B is probably due in part to the intumescent nature of the filler (see figures 14 and 15) which swells and produces voids in the uncharred material.

None of the formulations containing mixtures of nonyl phenolic-standard phenolic-Syl-Kem 90 and asbestos fiber rated very high in insulation performance (Table XXII). However, several asbestos-filled nonyl phenolic-Syl-Kem 90 formulations (7-16A, 7-16B, 7-16C) had acceptable char rates (see motor firing M-300, Table XXIV).

When the standard phenolic-Syl-Kem 90 resin (1:1 ratio) was filled with 45 per cent potassium oxalate (formulation 7-19F), the char rate was quite inferior to U. S. Rubber 3015 (firing PYB-5, Table XXII). However, when this same resin composition was filled with 62 per cent potassium oxalate (formulation 7-19G), the char rate was identical to U. S. Rubber 3015 (motor firing M-299, Table XXIII).

D. POLYURETHANE RESINS

1. Internal Flexibilization of Polyurethane Resins

A formulation consisting of 23 parts of toluene diisocyanate and 77 parts of castor oil was cured at 90°C for 25 minutes and post-cured at 125°C for 90 minutes. The cured resin was very flexible but had low tensile strength.

2. Oxyacetylene-Torch Testing of Filled Urethane Resins

To get a feeling on how the urethane resins might perform as a class, two commercially available materials* were tested in the oxyacetylene torch (Table XXVI). The structure of the polyurethane is apparently proprietary; the filler appears to be partly crocidolite asbestos fiber. In general, the performance of these materials was inferior to the epoxy resins.

* Thermothanes, Thiokol Chemical Corporation

Table XXVI

Oxyacetylene Torch Test Results for Filled Polyurethane Resins

| Material ^a | Density (gm/cu cm) | Erosion Rate (mil/sec) | Char Rate (mil/sec) | Temperature Index | | Weight Loss (per cent/sec) | Weight Loss (gm/sec) |
|-----------------------|-----------------------|---------------------------|------------------------|--------------------|--|-------------------------------|-------------------------|
| | | | | 1400°F (sec/in) | | | |
| Thermothane 3A | 1.37 | >8.63 ^b | >8.63 | 108 | | 1.17 | 0.275 |
| | | >8.24 | >8.24 | 111 | | 1.17 | 0.282 |
| | | Avg >8.44 | Avg >8.43 | Avg 110 | | Avg 1.17 | Avg 0.279 |
| Thermothane 3B | 1.41 | 7.31 | 6.88 | 120 | | 1.36 | 0.340 |

a. Cured 1 hour at 300°F and 3,000 psi.

b. Specimens eroded and charred completely; only a minimum value can be reported.

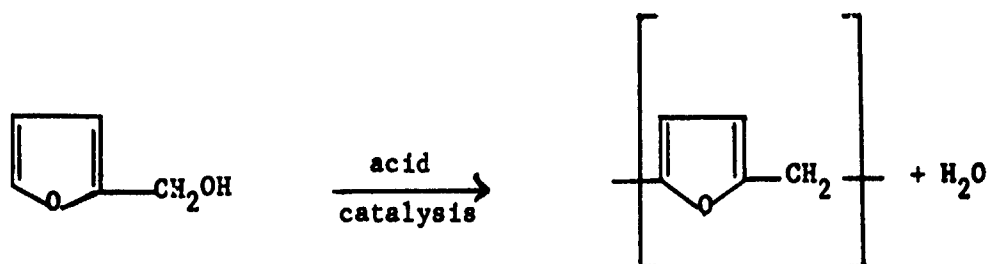
3. Motor Firing Tests of Filled Polyurethane Resins

Four asbestos-filled polyurethane resins were tested in the same peripheral slab static-motor firing (B-35) as the epoxy resins in Table XIV on page 34. A direct comparison of the two types of materials can be made. The test results for the polyurethane materials are listed in Table XXVII and a photograph of the charred materials is shown in Figure 12.

These results show that as a class the polyurethanes exhibit good insulation performance. The commercially available 41 RPD is one of the best performing rigid insulations in use today; and all of the polyurethanes had better char rates. Of particular interest in this series is the low density of PUX-400.

E. FURAN RESINS

Pure furan resins are thermosetting resins derived from the acid catalysis of furfuraldehyde or furfuryl alcohol. Intermediate or partially polymerized furan resins are also available which upon further reaction yield infusible products. The furfuryl alcohol polymerization reaction can be represented in its simplest form as follows:



A preliminary study of the effect of various acidic catalysts on the polymerization reaction was begun. It was thought that if organic acids were used as catalysts, they might also act as plasticizers and provide flexibility in the cured resin. The results of the work to date

Table XXVII

Peripheral-Slab Moto: Firing of Asbestos-Filled Polyurethane Resins
(Firing B-35)^a

| Code Number | Material | Filler | Density (gm/cu cm) | Char Rate (mil/sec) | Char Rate X Density |
|----------------|--|-------------------------------|-----------------------|------------------------|---------------------|
| Ru 126 | Thermothane 3A ^b | Asbestos | 1.37 | 4.5 | 6.2 |
| Ru 127 | Thermothane 3B ^b | Asbestos | 1.41 | 4.3 | 6.1 |
| PUX 400 | 21.45% Hylene M 36.83% polypropylene 2025 ^c 38.14% castor oil 3.58% Araldite 502 | 40% asbestos fiber (3R100) | 1.06 | 4.1 | 4.3 |
| XXVIII-D | 23% toluene diisocyanate 77% castor oil | 40% asbestos fiber (3R100) | 1.35 | 4.1 ^e | 5.5 |
| Ru 146 | U. S. Rubber 3015 ^d | -- | 1.24 | 3.2 | 4.0 |
| 41 RPD | Asbestos-phenolic resin ^d | 70 to 75 | 1.5 | 5.0 | 7.5 |

a. Length of firing: 46.3 sec; flame temperature: 6500°F; high pressure; quenched with nitrogen.

b. Commercially available polyurethane from Thiokol Chemical Corporation.

c. Polyurethane developed at Atlantic Research Corporation.

d. Included as a good commercially available insulation.

e. This char rate was incorrectly reported in a previous Quarterly Progress Report (January, 1962).

are recorded in Table XXVIII. Some flexibility was achieved when 10 parts of furfuryl alcohol were mixed with 2 parts of isosebacic acid and cured at 75°C for 70 hours followed by 2 hours at 150°C.

Preliminary attempts to modify and flexibilize the furan resins with Thiokol liquid polymers were not successful. Equal parts by weight of furfuryl alcohol and Thiokol liquid polymers LP-3, -8, -32, or -33 were mixed with sufficient catalyst TP to complete the polymerization. The mixtures were cured at 75°C for 7 hours followed by heating for 5 hours at 150°C. All of the materials described were hard and brittle.

Flexible resins which contained 20 parts by weight of furfuryl alcohol or furfuraldehyde, 20 parts of standard phenolic resin, and 60 parts of Syl-Kem 90 were obtained after curing at 75°C for 24 hours followed by post-curing at 150°C for 3 hours. Further work is planned in this system. The phenol-furfuraldehyde resin will be prepared and its reaction with Syl-Kem 90 studied as a possible means of flexibilizing furan resins.

Table XXVIII
Acid Catalysis of Furfuryl Alcohol Polymerizations

| Resin Composition (parts by weight) | Curing Cycle | | Remarks |
|---|---------------------|--------------|--|
| | Temperature (°C) | Time (hr) | |
| 10 furfuryl alcohol 0.5 catalyst TS ^a | 75 150 | 24 2 | Good cure, flexible, brittle. |
| 10 furfuryl alcohol 0.5 catalyst TP ^a | 75 150 | 24 2 | Good cure, flexible, brittle. |
| 10 furfuryl alcohol 2 oxalic acid | 75 | 0.25 | Hard, brittle. |
| 10 furfuryl alcohol 2 citric acid | 75 | 24 | Brittle. |
| 10 furfuryl alcohol 2 pelargonic acid | 75 150 | 70 2 | Incomplete cure, brittle. |
| 10 furfuryl alcohol 2 acrylic acid | 75 | 70 | Brittle. |
| 10 furfuryl alcohol 2 methacrylic acid | 75 | 70 | Brittle. |
| 10 furfuryl alcohol 2 hexafluoropentenediol | 75 150 | 70 2 | Incomplete cure, brittle. |
| 10 furfuryl alcohol 2 isosebacic acid | 75 150 | 70 2 | Incomplete cure, slightly flexible. |

a. Catalyst TS and catalyst TP are commercially available furan catalysts (Furane Plastics - supplier).

III. SUMMARY OF INSULATION WORK

During the two years of this program, flexible epoxy, phenolic, and urethane resins were developed for insulation studies. Asbestos-filled moldings were readily prepared and evaluated in insulation performance by the oxyacetylene torch and actual static-motor firings. With several of the resins, other fillers and composite fillers were examined.

Considerable effort was devoted to the preparation of flexible melamine resins. Although a few flexible formulations were developed, asbestos-filled moldings could not be prepared.

Initial studies were started with the furane resins.

The best insulators developed to date in this program are summarized in Table XXIX below. The better commercially available motor-case insulations have char rates of approximately 3.0 mil/sec. The density of the material is also an important consideration in selection of insulation for missile applications. Other properties being equivalent (aging, mechanical, etc.), the product of char rate and density allows a numerical rating of the materials according to over-all effectiveness, with the lowest number rated the best. However, in practice, selection of the material is actually more complicated. For example, material A with a char rate of 2 and a density of 4 would be selected over material B with a char rate of 4 and a density of 2, although both materials have a char rate-density value of 8. The weight of insulation used would be the same for both materials, but material A would be only half as thick as B and thus would allow more propellant in a motor of given size. If material A had a char rate of 2.5 instead of 2, its char rate-density value would be 10 and it would add more weight than B to the missile for a given insulation requirement. However, A would still occupy less volume than B on the inside of the motor and thus allow more propellant to be placed in a motor of fixed size. If the propellant has sufficient energy, the additional weight of insulation B could be overcome by the additional amount of propellant placed in the motor. At present, no attempt will be made to correct for this additional variable in selection of an insulator.

It should be emphasized that the data in Table XXIX represent only a limited number of tests, that char rate differences of 0.5 mil/sec are probably not significant, and that differences in the propellant used, time duration of the motor firing, pressure, and specimen position make it difficult to compare materials tested in different motors. U. S. Rubber 3015 insulation was used as a comparative standard and represents one of the best commercially available materials.

Table XXIX

Summary of Best Insulation Developed to Date Under this Program

| Code Number | Formulation | Density (gm/cu cm) | Motor Firing Conditions | | | Char Rate (mil/sec) | Char Rate x Density (mil-gm/sec-cu cm) |
|-------------|--|--------------------|-------------------------|------------------------|------------|------------------------|--|
| | | | Position | Flame Temperature (°F) | Time (sec) | | |
| XIV-F | 40% castor oil-modified Guardian, varying NMA | 1.41 | convergent | 6500 | 43.6 | 3.0 (3.2) ^a | 4.2 (4.0) ^a |
| X-B | Araldite DP-437/NMA (1:1 ratio) | 1.52 | convergent | 5600 | 66.1 | 2.4 (2.6) | 3.6 (2.1) |
| X-A | Araldite DP-437/NMA (1:1 ratio) | 1.52 | peripheral | 5600 | 62.3 | 2.4 (2.7) | 3.6 (3.3) |
| XXXI | 40% castor oil-modified Guardian, varying NMA | 1.32 | convergent | 6500 | 34.8 | 1.1 | 1.3 |
| 7-12-B | Syl-Kem 90-modified standard phenolic formaldehyde resin | 1.52 | convergent | 5600 | 30.2 | 2.6 (2.3) | 4.0 (2.8) |
| 7-19-E | Syl-Kem 90-modified standard phenolic formaldehyde resin | 1.50 | convergent | 6500 | 46.0 | 3.3 (3.5) | 5.0 (4.3) |
| 7-19-E | Syl-Kem 90-modified standard phenolic formaldehyde resin | 1.50 | convergent | 5600 | 68.1 | 2.1 (3.1) | 3.1 (3.8) |
| 7-16-B | Syl-Kem 90-modified nonyl phenolic formaldehyde resin | 1.37 | convergent | 5600 | 66.1 | 2.7 (2.6) | 3.7 (3.2) |

a. The values in parentheses are for U. S. Rubber 3015 insulation tested at the same time.

IV. FUTURE WORK

During the next year of this program, the following general areas of work will be emphasized:

- (1) Static-motor testing of filled resins;
- (2) development of flexible melamine, furan polyester and urethane resins; and
- (3) determination of the mechanical properties of the better-performing filled resins.

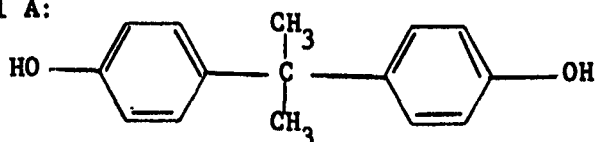
Much less emphasized will be the development of new flexible epoxy and phenolic resins. With a few of the better-performing resins, other fillers (asbestos felt, ceramic microballoons, low-temperature decomposing salts) will be studied in addition to the asbestos fiber. No oxyacetylene-torch testing is planned.

APPENDIX

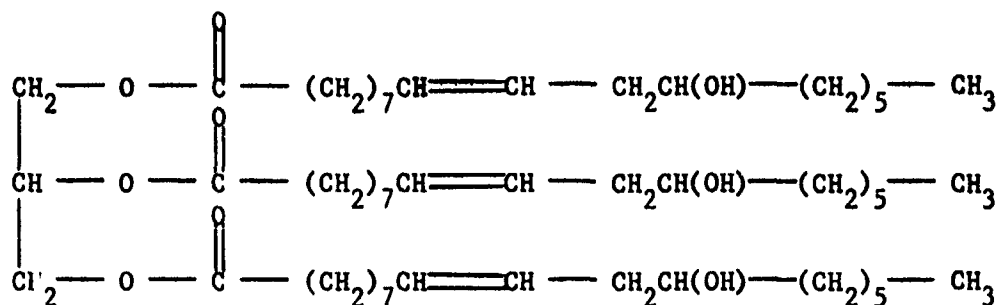
Formulary

1. Araldite 502 (Ciba): Liquid epoxy resin, epoxy equivalent 250.
2. Araldite DP-437 (Ciba): An inherently flexible, liquid epoxy resin, epoxy equivalent 285.
3. Aroclor 1248 (Monsanto): A polychlorinated biphenyl.
4. Asbestos fiber 3R100 (H. K. Porter Co.): Chrysolite asbestos fibers.
5. Asbestos powder 7MS-1 (Powhatan Mining Co).
6. B2620 (Union Carbide, Bakelite): A-stage, phenol-formaldehyde resin.
7. BDMA (Miles Chemical Company): Benzyldimethyl amine.

8. Bis-phenol A:



9. Castor oil (The Baker Castor Oil Co.):

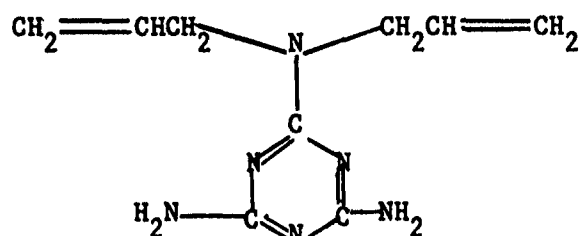


10. Castor oil-modified Guardian (Atlantic Research Corp.)

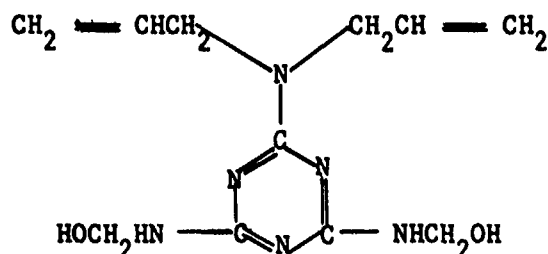
- (a) 30% modification
 - 1.00 part Epon 828
 - 1.13 parts NMA
 - 0.91 part castor oil
- (b) 35% modification
 - 1.00 part Epon 828
 - 1.20 parts NMA
 - 1.19 parts castor oil

- (c) 40% modification
1.00 part Epon 828
1.29 parts NMA
1.52 parts castor oil

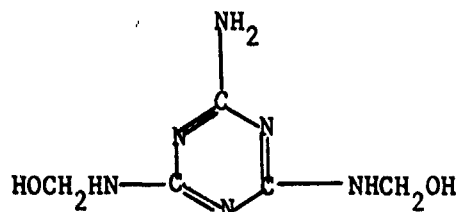
11. Diallyl melamine (American Cyanamid):



12. Dimethylol diallyl melamine (synthesized):



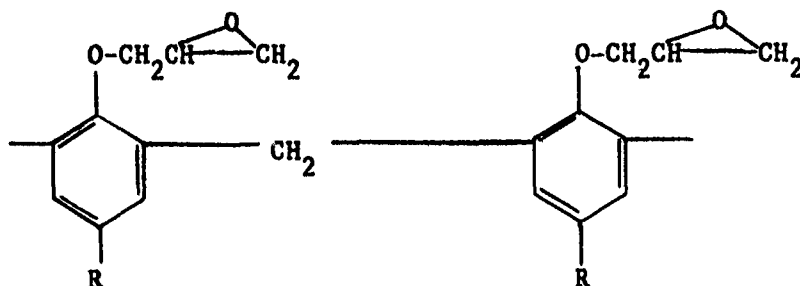
13. Dimethylol melamine (American Cyanamid):



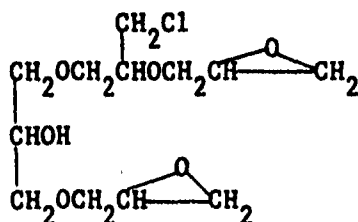
14. EM206 (Thiokol): Structure proprietary, appears to be a hydroxy-terminated polyester; epoxy modifier.
15. EM207 (Thiokol): Structure proprietary, appears to be a hydroxy-terminated polyester of higher molecular weight than EM206; epoxy modifier.
16. Empol 1014 (Emery): A mixture of 95 per cent of a C₃₆ diacid, 4 per cent of a C₅₄ triacid, and 1 per cent of a monobasic acid.

17. Epichlorohydrin: $\text{ClCH}_2\text{CH} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH}_2 \end{array}$

18. Epiphen 825 (Borden Chemical): Liquid, Novolac epoxy resin.

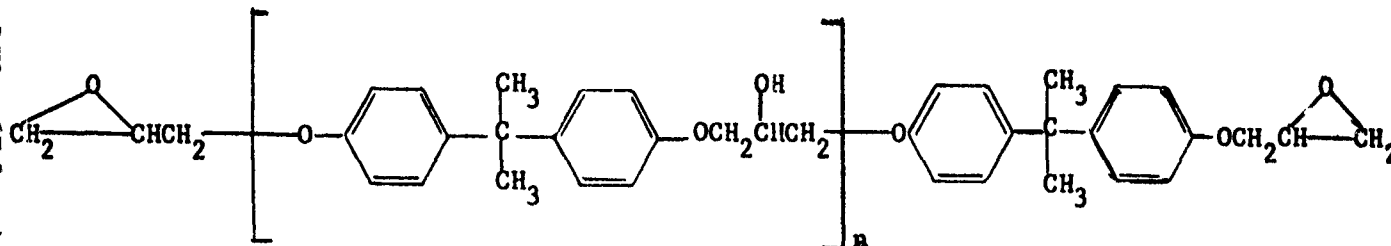


19. Epon 812 (Shell Chemical Corp.): Liquid epoxy resin; epoxy equivalent 140-160.



20. Epon 815 (Shell Chemical Corp.): Liquid epoxy resin; epoxy equivalent 175-195; similar in structure to Epon 828 but to which a reactive diluent has been added.

21. Epon 828 (Shell Chemical Corp.): Liquid epoxy resin; epoxy equivalent 180-195.

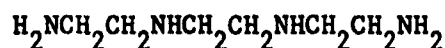


22. Gen-Gard V-44 (The General Tire and Rubber Co.): Asbestos-filled butadiene-acrylonitrile rubber insulation.

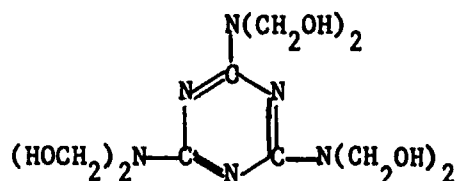
23. Guardian (Atlantic Research Corp.): This material was referred to previously as Standard Guardian. Its formulation is:

10 parts Epon 828
9 parts NMA

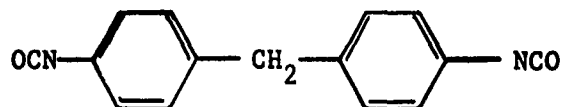
24. Hardner 951 (Ciba): Triethylene tetramine



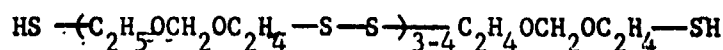
25. Hexamethylol melamine (synthesized):



26. Hylene M (Du Pont):

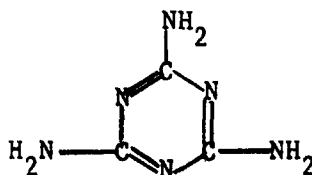


27. LP-8 (Thiokol): A liquid polysulfide with the following average structure and in which some side mercaptan groups occur occasionally:

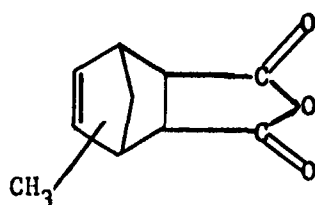


28. Magnesium carbonate (Fisher, U. S. P. Powder).

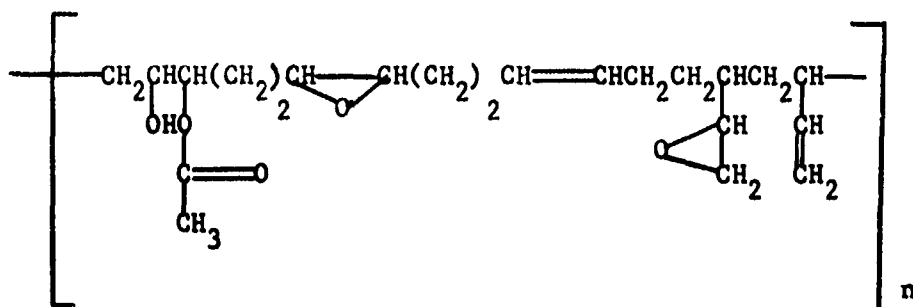
29. Melamine (American Cyanamid):



30. Nadic methyl anhydride (National Aniline):



31. Oxiron 2000 (Food Machinery and Chemical):
Epoxidized polyolefin:

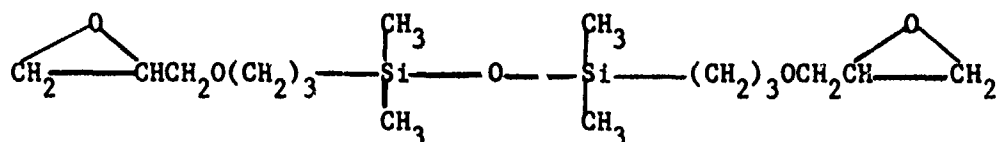


32. Plurocol TP-440 triol (Wyandotte): Structure unknown.

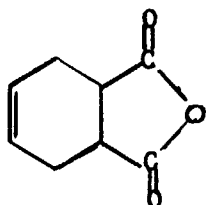
33. Potassium oxalate (Fisher, Certified): $K_2C_2O_4 \cdot H_2O$

34. QZ-8-0914 (Dow Corning): Technical grade of Syl-Kem 90.
See structure below.

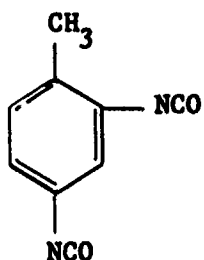
35. Syl-Kem 90 (Dow Corning): A liquid epoxy resin.



36. THPA, tetrahydrophthalic anhydride (Allied Chemical):



37. Toluene diisocyanate (Du Pont)



38. U. S. Rubber Co.'s 3015 insulation (U. S. Rubber): One of the best commercially available insulations. Used as comparative standard in this work. Potassium oxalate filler.
39. Versamid 140 (General Mills): A polyamide with reactive amine groups.
40. XR2000 (General Mills): Structure unknown. An epoxy modifier which appears to contain reactive amino groups.